A. Non-relativistic theory

(1) Indeterminacy and complementarity: In the case of diffraction by a grating the classical wave theory explanation is based on the superposition principle and is in consonance with observation. It holds also for arbitrary small intensities of the incident light and hence also true for a radiating atom. On the corpuscular standpoint the process consists first in emission from the radiating atom, then in a scattering with recoil at the grating and finally an emission at the place of observation. The fact that the light quantum comes only at specified places behind the grating depends on the presence of all the atoms of the grating. If we now assume that it is possible to specify the places of the grating which are hit by the quantum, without altering the character of the diffraction phenomena, one is led to insurmountable difficulties. The behaviour of a light quantum at any moment must be connected with the positions of the atoms of the grating as a whole, and this makes it impossible to associate a light quantum with a classical wave field. In fact there is no wave-field having the property that its intensity vanishes everywhere on the grating except at one place, and in addition that there are only determinate directions for the diffracted rays in it. It is only possible to realise either the one or the other of these properties through a wave field. Then to obviate a contradiction with the superposition principle, the assumption that only one place of the grating is hit by the quantum would mean that all the other lines of the grating have no part in the diffraction phenomenon which is equivalent to denying the presence of the grating itself. The difficulty of reconciling the wave and corpuscular aspects arises not merely in diffraction but generally in

all interference phenomena. Light-waves are propagated in different directions and thereby arises phase-differences and further the waves might arrive at the same point. To postulate that a light-quantum takes at a place only one of these paths and no other is contrary to observed interference phenomena. The wave-corpuscle duality can be formulated in general terms thus:-

All statistical properties given by results of measurement on a light-quantum, which are consequences of the knowledge of other (earlier or later) measurements, are uniquely determined by specifying a wave field associated with these results of measurement.

It is supposed that this wave-field is generated by the superposition of plane waves of different directions and wave lengths and consequently one speaks of wave packets. Thus on this association we can say that the knowledge that a light quantum is found in a certain region of space-time is contained in the statement that the amplitude of the corresponding wave field is sensibly different from zero only inside the concerned region of space-time.

Let the complex phase of a plane wave be given by

$$e^{i\left(\sum_i R_i x_i - \omega t\right)} \qquad (1)$$

where $\vec{R}$ has the direction of the wave normal and has the magnitude $2\pi/\lambda$, and ω (ν) is equal to 2π times the frequency. ω is an uniquely determined function of R_1, R_2, R_3 depending on the nature of the wave, and for electromagnetic waves in a vacuum

$$\sum_i R_i^2 = \omega^2/c^2 \qquad (2)$$

In the most general wave field a component of any field strength can be represented as

$$u(x_i, t) = \int A(\vec{R})\, e^{i\left(\sum R_i x_i - \omega t\right)}\, dR_1\, dR_2\, dR_3 \qquad (3)$$

It can be shown from elementary considerations that if $u(x_i, t)$ and $A(\vec{R})$ be appreciably

simultaneously different from zero, at a given time, respectively in the regions $(\Delta x_1, \Delta x_2, \Delta x_3)$ and $(\Delta k_1, \Delta k_2, \Delta k_3)$, then the three products $\Delta x_i \Delta k_i$ cannot be arbitrarily small but must be of the order 1, i.e.

$$\Delta x_i \, \Delta k_i \sim 1 \qquad (4)$$

Similarly for a fixed space point $(x_1 x_2 x_3)$ and a fixed point $(k_1 k_2 k_3)$ in the k-space, one has the relation

$$\Delta t \, \Delta \omega \sim 1 \qquad (4')$$

In the corpuscular notion of light quantum the essential quantities are the momentum $\vec{p}$ in the direction of motion and the energy E. The wave-corpuscle duality is expressed, taking the definition of $\vec{k}$ and eq. (2) into consideration, by taking the magnitude of p as $\hbar\omega/c$ and of E as $\hbar\omega$. Thus

$$\vec{p} = \hbar \vec{k} \; ; \quad E = \hbar\omega \qquad (I)$$

and (4) & (4') becomes

$$\Delta p_i \, \Delta x_i \sim \hbar \; ; \quad \Delta E \, \Delta t \sim \hbar \qquad (II)$$

These are Heisenberg's uncertainty relations, and the derivation here given is due to Bohr.

Since measurements on light quanta are made with the help of observations on the interaction of light and matter, if we assume (II) to hold for light quanta and if we also assume principles of conservation of momentum and energy to be strictly true (II) must also hold for material bodies of any sort; (this is the meaning of saying that (II) holds for light quanta (See later)) The wave-corpuscle duality also implies the validity of (I) for material particles and this is the content of de Broglie's concept of matter waves. We can also talk of the diffraction of matter waves on the same footing as diffraction of light waves. Only the relation between wave number and frequency is not given by (2), which is valid for light waves, but recourse to the relativistic relation between momentum & energy viz

$$\frac{E^2}{c^2} = m^2 c^2 + \sum_i p_i^2 \qquad (5)$$

(m = rest-mass of the particle). According to (I) this gives for matter waves

$$(5') \quad \frac{\omega^2}{c^2} = \frac{m^2 c^2}{\hbar^2} + \sum_i k_i^2 = \frac{\omega_0^2}{c^2} + \sum_i k_i^2 \qquad (\omega_0 = \frac{mc^2}{\hbar})$$

The relation (I) is relativistic invariant since $(\vec{p}, \frac{iE}{c})$ as also $(\vec{k}, i\omega/c)$ are components of a four-vector. (5) & (5') are also relativistic invariant. For $m = 0$, these go into corresponding eqns for photons.

The corresponding quantity to particle velocity is group velocity of the wave. The former is given by $v_i = \frac{\partial E}{\partial p_i}$ (Cf. Hamilton's Canonical eqn), and the latter by $\partial\omega/\partial k_i$ and the equivalence of these is immediate in virtue of (I).

In case of the law (5), $v_i = \frac{c^2 p_i}{E}$ and substituting in (5) gives

$$\left.\begin{aligned} E &= \frac{mc^2}{\sqrt{1 - v^2/c^2}} \\ p_i &= \frac{m v_i}{\sqrt{1 - v^2/c^2}} \end{aligned}\right\} \qquad (5, 6)$$

the well known eqns for energy and momentum in terms of velocity.

In the non-relativistic case, where $|p| \ll mc$

$$\frac{E}{c} = \sqrt{m^2c^2 + \Sigma p_i^2} = mc\left(1 + \frac{1}{2m^2c^2}\Sigma p_i^2\right)$$

$$\text{or } E = mc^2 + \frac{1}{2m}\Sigma p_i^2 \qquad (8)$$

$$\text{also } \omega = \omega_0 + \frac{\hbar}{2m}\Sigma k_i^2 \qquad (8')$$

Also note the possibility of the square root taking a -ve sign. Changing the zero point of energy & ω resp by $E' = E - mc^2$, $\omega' = \omega - \omega_0$.

$$\left.\begin{aligned} E' &= \frac{1}{2m}\Sigma p_i^2 ; \\ \omega' &= \frac{\hbar}{2m}\Sigma k_i^2 \\ v_i &= \frac{p_i}{m} = \frac{\hbar k_i}{m} \end{aligned}\right\} \qquad (11)$$

and $$\lambda = \frac{2\pi}{|k|} = \frac{2\pi\hbar}{mv} = \frac{h}{mv} \qquad (12)$$

which is de Broglie's famous formula for material waves.

Complementarity: The uncertainty relation (II) for matter shows that one cannot apply the usual classical kinematics for material particles, for this relation asserts that every exact knowledge of the position of a particle means at the same time an indeterminacy in the knowledge of the momentum. This indeterminacy should be distinguished from ambiguity (unbekanntheit) - Example of light quantum through two apertures — In case of uncertainty the experimental arrangement is quite definite. By indeterminacy one means that every arrangement to measure a certain property prevents the measuring of the influence of an earlier knowledge of the system on the assertion of the possible future state of the system. In other words the measurement itself transforms the system to a new state

Hence in order to determine the position and momentum of a system one must employ mutually exclusive experimental arrangements. The influence on the system of the measuring apparatus is such that within the limits of the uncertainty relation, the application of the knowledge of position (momentum) at an earlier time to an assertion of the result of measurement of position (momentum) at a later time is forbidden (lost). Thus, in general, when the applicability of one classical notion is in an exclusive relationship to that of another notion (for e.g. position and momentum coordinate of a particle) we call these notions complementary to each other. In analogy to the term "Relativ Theory of Relativity" one might call quantum mechanics as "Theory of Complementarity"

According to this conception the unique objectivisability of physical

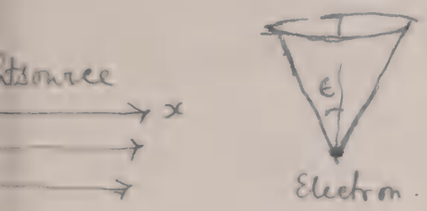
phenomena, and hence the ~~the~~ their causal space time description are also lost. It becomes arbitrary at which place one has to separate the means of observation and the phenomena. It can nevertheless be shown that one can give a statistical characterisation and a statistical laws can be obtained that for a system without contradictions.

(2) Measurement of position and momentum: To observe the position of a material particle one considers this as subject to some external action and the result is observed. Such an agency is given by the scattering of light. Let us imagine the (x,y) plane illuminated with the help of a wave train of limited length such that a point $(x_0 y_0)$ of the plane is illuminated at a definite time t_0. This time has an "interval play" Δt which cannot be less than $1/\nu$ when ν is the mean frequency of the light. By employing the waves of the smallest possible wave-length Δt can however be made as small as possible. The accuracy of the determination of position is limited by the optical arrangements used. Thus for eg. in case of a microscope

$$\Delta x \sim \lambda'/\sin\epsilon \qquad (13)$$

where λ' is the wave length of the scattered light (which may be different from that of the incoming radiation) while ϵ is half the aperture angle of the lens objective lens. The direction of the scattered quantum has an indeterminacy in principle within this angle, and accordingly the component of the momentum of the material particle in the x-direction after the impact is indeterminate by

$$\Delta p_x \sim \frac{h}{\lambda'} \sin \epsilon \qquad (14)$$



which gives a confirmation of the uncertainty relation

$$\Delta p_x \, \Delta x \sim h.$$

According to (13) it possible to make $\Delta x \to 0$ by making $\lambda' \to 0$

but as found in the Compton effect there is a maximum ν' and a minimum λ' ($= c/\nu'$) determined by conservation of energy and momentum such that

$$\left.\begin{aligned} \nu' &\sim \frac{E}{h} = \frac{m_0 c^2}{h} \frac{1}{\sqrt{1 - v^2/c^2}} \\ \lambda' &\sim \frac{hc}{E} = \frac{h}{m_0 c} \sqrt{1 - v^2/c^2} \end{aligned}\right\} \qquad (15)$$

We might neglect very small scattering angles since from a geometrical point of view, these are not significant for the determination of position. Thus for the maximum accuracy obtainable for position determination with the help of the experiments discussed, one has

$$\left.\begin{aligned} \Delta x &\sim \frac{hc}{E} = \frac{h}{m_0 c} \sqrt{1 - v^2/c^2} \\ \Delta t &\sim \frac{1}{\nu'} \sim \frac{h}{E} = \frac{h}{m_0 c^2} \sqrt{1 - v^2/c^2} \end{aligned}\right\} \qquad (16)$$

From the second of these it follows that the duration of the scattering process i.e. the time within which the interaction between light-quantum and material particles is determined can never be essentially less than the light periods of the incoming + incident and scattered radiation. This duration is ~~just because~~ of importance in measuring position since along with it is determined the applicability of results of measurement for predicting later measurements of position. In this sense there appears a possibility of repetition of a measurement of position at a later instant of time. Let us once again determine

in a single case, but one could determine by repeated experiments a mean position $\bar{x}(t_0+\tau)$ with a certain mean error $\Delta = \sqrt{\overline{(\Delta x)^2}}$. Then by making τ arbitrarily small one can make $\bar{x}(t_0+\tau) - \bar{x}(t_0)$ as also $\Delta(t_0+\tau) - \Delta(t_0)$ arbitrarily small. Had the time-point of the first measurement of position been completely undetermined (indeterminate it could not have been possible to predict the result of another measurement, and this would have had no physical interest.

The limits of accuracy given by (16) for determination of position is of importance in the first place for nuclei and electrons since for atoms as a whole their dimension is in general large compared with their value of $\hbar/mc$. whether however these limits have, for the former particles, a significance of principle or whether they can be evaded by indirect methods is a question which cannot be answered by merely elementary considerations but require a careful examination on the basis of relativistic quantum mechanics. To avoid these complications regarding the atomistic structure of lenses, mirrors and aberrations, one can assume make the positive assumption that the notion of the position of a material particle at a specific time has also a meaning outside the region of validity of classical mechanics. The determination of position is accordingly always possible with an accuracy greater than the wave length of matter waves

$$\lambda_m = \frac{h}{|p|} = \frac{\hbar}{mv}\sqrt{1-v^2/c^2}$$

since according to (16)

$$\Delta x \sim \lambda_m \cdot v/c \qquad (17)$$

At least in non-relativistic quantum theory where $v \ll c$, it is natural to make the following assumption: In every state of a system, free of a single force free particle there exists at every instant t a probability $W(x_1, x_2, x_3)\,dx_1\,dx_2\,dx_3$ that the

~~quanta~~ particle is found at the position (x_1, x_2, x_3) inside the region $dx_1\, dx_2 dx_3$.

This fundamental assumption is neither self-evident nor a direct consequence of the uncertainty relation (II). It will be evident later that a specification of the position of a light-quantum outside the limits of classical geometrical optics is not possible. The position of a light quantum cannot be determined more accurately than by an amount equal to the wave length of the light, and that in a time not smaller than the light period. The uncertainty relation postulated for light quanta do not refer to the position and momentum of a light quantum. It simply means that if a beam of light is such ~~that~~ as to give an image of a point (electron) in the x-direction, say, with an accuracy Δx, the x-component of the momentum of this light-beam is uncertain by an amount $h/\Delta x$. There is therefore no light-quantum density analogous to the density of material particles. The analogy between light and matter which was pointed out at the beginning does not appear to be so broad as it would appear. It is exhausted by the fact that the fundamental relation (II) between energy - momentum, and frequency - wave number is valid for light quanta as well as material particles.

In the formulation of the above fundamental postulate we have sign distinguished the space coords from the time-coordinate since the former are thought of as being determined within dx_i while t is exactly known. ~~was~~ Actually however, as we have seen, the time instant cannot be fixed more exactly than by $\Delta t = \Delta x/c$ when the order of magnitude of the error determination in x is Δx. Only in the limit of the non-relativistic theory where, so to say, c can be considered infinitely great there appears a possible idealisation ~~to neglect~~ and one could neglect Δt for a fixed Δx.

Let us now consider the question of measurement of momentum of a particle. As shown by Bohr we can again use the scattering experiment since the Doppler effect in a given direction of the scattered light allows us to get information about the velocity of the material particle. The time of interaction T is given by

$$\Delta\nu' = 1/T \tag{18}$$

and, unlike as in the case of measurement of position, it is here convenient to choose this a large interval. Let us consider for simplicity the process in which the particle moves in the $+x$ direction (so that $p_y = p_z = 0$) and that the light which falls on the particle in the $-x$ direction is scattered in the $+x$ direction. This gives

$$-\frac{h\nu}{c} + p_x = p_x' + \frac{h\nu'}{c}$$

or, $$p_x' = p_x - \frac{h\nu}{c} - \frac{h\nu'}{c} \tag{19}$$

and $$h\nu - h\nu' = E' - E \quad (E + h\nu = E' + h\nu') \tag{20}$$

Since ν is given an exact determination of ν' gives a certain knowledge of p_x (and p_x'). To find the connection between Δp_x and $\Delta\nu'$, we have first to calculate $\partial\nu'/\partial p_x$ from (20) wherein, according to (19) p_x' is considered a function of p_x and ν' with ν constant. Remember that

$$\frac{\partial E'}{\partial p_x'} = v_x' \quad ; \quad \frac{\partial E}{\partial p_x} = v_x$$

(which is also true in the relativistic case) we find (from (20))

$$-h\frac{\partial\nu'}{\partial p_x} = -h\frac{\partial\nu'}{\partial p_x} = \frac{\partial E'}{\partial p_x} - \frac{\partial E}{\partial p_x} = \frac{\partial E'}{\partial p_x'}\cdot\frac{\partial p_x'}{\partial p_x} - \frac{\partial E}{\partial p_x} = v_x'\frac{\partial p_x'}{\partial p_x} - v_x$$

but from (19), $\dfrac{\partial p_x'}{\partial p_x} = 1 - h\dfrac{\partial\nu'}{\partial p_x}$; eliminating $\partial p_x'/\partial p_x$ we have

$$h\frac{\partial\nu'}{\partial p_x}\left(1 - v_x'/c\right) = v_x - v_x'$$

For the uncertainty we have firstly

$$h\,\Delta\nu' = \frac{v_x - v_x'}{1 - v_x'/c}\,\Delta p_x$$

From the conditions of impact, which is a head-on collision we see that for small ν, v_x' is nearly equal to v_x, and decreases as ν increases, finally becoming negative and tending to $-c$ when ν becomes infinitely great. The denominator varies accordingly from $1 - v_x/c$ to 2, and hence up to order of magnitude

$$h\,\Delta\nu' \sim (v_x - v_x')\,\Delta p_x \tag{21}$$

or according to (18),

$$\Delta p_x \sim \frac{h}{(v_x - v_x')\,T} \tag{22}$$

on the other hand for the indeterminacy in principle for the position of the particle

$$\Delta x \sim (v_x - v_x')\,T$$

since it is indeterminate at what instant of time inside the interval T the velocity changes. We thus find the uncertainty relation

$$\Delta p_x\,\Delta x \sim h$$

again in confirmation. Equation (22) shows that one can measure the impulse of the particle even in an arbitrarily small interval time when the (determinate) velocity change in the process can be arbitrarily large. But this change cannot in reality be greater than $2c$, so that in order of magnitude

$$\Delta p_x = \frac{h}{c\,\Delta t} \tag{23}$$

Here we have written Δt in place of T so as to denote that T gives the uncertainty at what instant of time the value p_x is realised. The results (22) and (23) which give lower limits for the error Δp_x are independent of the direction of the velocity of the material particle.

In the case of a ~~force~~-free particles the limitation on the exactness of the measurement of momentum by the time-interval T is not essential since the momentum of the particle is here a time constant of time. We might accordingly assume: For every state of a system, firstly in the case of a free particle, there exists a probability $W(p_1 p_2 p_3)\,dp_1 dp_2 dp_3$ that the momentum has the value $p_1 p_2 p_3$ inside the region $dp_1 dp_2 dp_3$ (this assumption holds good evidently for free radiation a light-quantum in case of free radiation).

The measurement of momentum is however is not in general "repeatable" inside its limit of exactness (22) because the appearance of a known change of momentum introduces great complications. Only when the T is chosen so large that, for given Δp_x, $(p_x' - p_x)$ can also be made small is it possible for a first measurement to lead to the same result as an immediately following one. In all cases however, for short time measurements, the result of a measurement is predictable from that of the preceding one. This fact is important for the question of measurement of momentum of interconnected particles where one has only a limited time at one's disposal for measurement.

(3) Wave function of a free-particle: we have now to introduce fundamental assumptions regarding $W(x_1 x_2 x_3)$ and $W(p_1 p_2 p_3)$ consistent with (I) and (II). We shall limit ourselves to the non-relativistic case, where

$$\omega = \omega_0 + \frac{h}{2m} \Sigma k_i^2 \qquad (8')$$

By this limitation light quanta are excluded from consideration, and the relativistic theory will be considered in Part B.

Let the wave function, as in (3),

$$\psi(x_i,t) = \frac{1}{\sqrt{(2\pi)^3}} \int A(\vec{k})\, e^{i[(\vec{k}\vec{x}) - \omega t]}\, dk_1\, dk_2\, dk_3 \qquad (24)$$

be built with the factor $1/\sqrt{(2\pi)^3}$ whose use will be evident later on. The conjugate complex function is

$$\psi^*(x_i,t) = \frac{1}{\sqrt{(2\pi)^3}} \int A^*(\vec{k})\, e^{-i[(\vec{k}\vec{x}) - \omega t]}\, dk_1\, dk_2\, dk_3 \qquad (24^*)$$

Using (I) these can be written as

$$\psi(x_i,t) = \frac{1}{\sqrt{(2\pi\hbar)^3}} \int A(\vec{p})\, e^{\frac{i}{\hbar}[(\vec{p}\vec{x}) - Et]}\, dp_1\, dp_2\, dp_3 \qquad (24')$$

$$\psi^*(x_i,t) = \frac{1}{\sqrt{(2\pi\hbar)^3}} \int A^*(\vec{p})\, e^{-\frac{i}{\hbar}[(\vec{p}\vec{x}) - Et]}\, dp_1\, dp_2\, dp_3 \qquad (24'^*)$$

$A(\vec{p})$ and $A(\vec{k})$ differ by a numerical factor such that $|A(p)|^2 dp_1 dp_2 dp_3 = |A(k)|^2 dk_1 dk_2 dk_3$.

This explains the term $1/\sqrt{(2\pi\hbar)^3}$ in (24') and (24'*). Let us put

$$\varphi(p) = A(\vec{p})\, e^{-\frac{i}{\hbar}Et} \qquad (25)$$

so that $\varphi(\vec{p})$ satisfies the equation

$$-\frac{\hbar}{i}\frac{\partial \varphi}{\partial t} = E\varphi = \left(E_0 + \sum \frac{p_i^2}{2m}\right)\varphi \qquad (26)$$

and we can write

$$\psi(x_i,t) = \frac{1}{\sqrt{(2\pi\hbar)^3}} \int \varphi(\vec{p})\, e^{\frac{i}{\hbar}(\vec{p}\vec{x})}\, d\vec{p} \qquad (24'')$$

and $$\psi^*(x_i,t) = \frac{1}{\sqrt{(2\pi\hbar)^3}} \int \varphi^*(\vec{p})\, e^{-\frac{i}{\hbar}(\vec{p}\vec{x})}\, d\vec{p} \qquad (24''^*)$$

[The Fourier Integral theorem can be written as

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} f(t)\, e^{iy(t-x)}\, dt$$

$\frac{1}{2\pi}\int_{-\infty}^{+\infty} f(x)\, e^{ixy}\, dx$, the integral theorem fixes

At once the reciprocal relation

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy\, e^{-ixy} \int_{-\infty}^{+\infty} f(t)\, e^{iyt}\, .dt$$

ie $f(x) = \int_{-\infty}^{+\infty} g(y)\, e^{-ixy}\, .dy$ [Hilbert-Courant. pub4 Bd. I, p. 64]

The reciprocal theorem could be extended to any number of variables.

As is known from the theory of Fourier series, the Completeness relation is invariant for a Fourier transforms. This gives

$$\int \psi^* \psi\, dV = \int \varphi^* \varphi\, dp$$

since ψ & φ are fourier transforms of each other]

The reciprocal relations give

$$\varphi(\vec{p}) = \frac{1}{\sqrt{(2\pi\hbar)^3}} \int \psi(x_i, t)\, e^{-\frac{i}{\hbar}(\vec{p}, \vec{x})}\, .dV \qquad (27)$$

$$A(\vec{p}) = \frac{1}{\sqrt{(2\pi\hbar)^3}} \int \psi(x_i, t)\, e^{-\frac{i}{\hbar}[(\vec{p}, \vec{x}) - Et]}\, dV \qquad (27')$$

$$A(\vec{k}) = \frac{1}{\sqrt{(2\pi)^3}} \int \psi(x_i, t)\, e^{-i[(\vec{k}, \vec{x}) - \omega t]}\, dV \qquad (27'')$$

Since ψ & φ are fourier transforms

$$\left.\begin{aligned} &\int \psi^* \psi\, dV = \int \varphi^* \varphi\, dp \\ \text{&} \quad &\int \varphi^* \varphi\, dp = \int A^* A\, dp. \end{aligned}\right\} \qquad (28)$$

The factor $\frac{1}{\sqrt{(2\pi)^3}}$ introduced in (24) was to have the completeness relation in this simple form.

On account of (8') we can show that ψ & ψ^* satisfy the differential eqns

$$-\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = \left(E_0 - \frac{\hbar^2}{2m}\Delta\right)\psi \qquad (29)$$

$$+\frac{\hbar}{i}\frac{\partial\psi^*}{\partial t} = \left(E_0 - \frac{\hbar^2}{2m}\Delta\right)\psi \qquad (29^*)$$

[from (24). $\otimes$ $-i\omega\psi \Rightarrow \frac{\partial\psi}{\partial t} = -i\omega\psi$

$$\frac{\partial\psi}{\partial x_i} = iK_i\psi \text{ , and } \frac{\partial^2\psi}{\partial x_i^2} = -K_i^2\psi$$

using (8') and (I) the eq^{ns} (29) & (29*) follow readily]

where $E_0 = \hbar\omega_0 = mc^2$ (6)

Conversely (24') is the general solution of the differential equation (29) where for each partial wave appearing in (24') the relation

$$E = E_0 + \frac{1}{2m}\Sigma p_i^2 \qquad (8)$$

obtained from (8') by using (I) is satisfied. Formally (29) is derived directly from (8) when we introduce operators operating on functions of space and time

$$\underline{\underline{E}} = -\frac{\hbar}{i}\frac{\partial}{\partial t} \; ; \; \underline{\underline{p_i}} = \frac{\hbar}{i}\frac{\partial}{\partial x_i} \qquad (30)$$

and then (8) is replaced by the identical operational equation identical with (29)

$$\underline{\underline{E}}\,\psi = \left(E_0 + \frac{1}{2m}\Sigma\,\underline{\underline{p_i}}^2\right)\psi \qquad (31)$$

This is also formally analogous to (26).

In the following we shall have occasion to use deal with general operators which possess the property of linearity

$$\underline{\underline{D}}(c_1\psi_1 + c_2\psi_2) = c_1\,\underline{\underline{D}}\,\psi_1 + c_2\,\underline{\underline{D}}\,\psi_2 \; . \qquad (32)$$

and the functions $\underline{\underline{D}}\,\psi$ have depend upon the same variables as the functions ψ.

Reverting to the special operators in (26) we notice that their correspondence with the quantities energy and momentum is only another expression for the forming of the fourier-integrals (24') by the transition $\psi(x_i, t) \rightarrow \varphi(\vec{p})$.

The physical significance of the functions introduced here is that they can be connected with the probabilities $W(x_i)$ and $W(p_i)$. It is essential that W cannot be negative in the first place, and secondly that at every instant of time

$$\int W(\vec{x})\, dx_1 dx_2 dx_3 = 1 \tag{33}$$

$$\int W(\vec{p})\, dp_1 dp_2 dp_3 = 1 \tag{33'}$$

must be valid. The simplest assumption for $W(x)$ satisfying these conditions is that $W(x)$ is a definite quadratic form of the values of (if needbe many) the functions ψ_ρ, ψ_ρ^*, $\cdots$ $(\rho = 1, 2, \cdots)$ each of which satisfies the equations (29) & (29*).

i.e. $$W(x) = Q(\psi_\rho, \psi_\rho^*) \tag{34}$$

(only the sequel can teach why we do not start with forms of fourth or higher orders). Also in order that the time constancy of $W(\vec{x})\, dx_1 dx_2 dx_3$ should result from (29) & (29*) we must necessarily put

$$Q(\psi_\rho, \psi_\rho^*) = \sum_\rho C_\rho \psi_\rho^* \psi_\rho \tag{35}$$

where C_ρ are positive real numbers. To see this we derive from (29) and (29*)

$$-\frac{1}{2}\frac{\hbar}{i}\frac{\partial}{\partial t}(\psi^2) = E_0 \psi^2 - \frac{\hbar^2}{2m}\sum \frac{\partial}{\partial x_i}\left(\psi \frac{\partial \psi}{\partial x_i}\right) + \frac{\hbar}{2m}(\operatorname{grad}\psi)^2$$

$$+\frac{1}{2}\frac{\hbar}{i}\frac{\partial}{\partial t}(\psi^{*2}) = E_0 \psi^{*2} - \frac{\hbar^2}{2m}\sum \frac{\partial}{\partial x_i}\left(\psi^* \frac{\partial \psi^*}{\partial x_i}\right) + \frac{\hbar}{2m}(\operatorname{grad}\psi^*)^2$$

but, $$\frac{\hbar}{i}\frac{\partial}{\partial t}(\psi\psi^*) = \frac{\hbar^2}{2m}\sum\frac{\partial}{\partial x_i}\left(\psi^*\frac{\partial\psi}{\partial x_i} - \psi\frac{\partial\psi^*}{\partial x_i}\right)$$

Accordingly neither $\int\psi^2 d\tau$ nor $\int\psi^{*2}d\tau$ nor any linear combination of them is at a time constant, but on the other hand (under the assumption that the wave functions vanish on the boundary of a sphere of large radius) one has

$$\int\psi\psi^* d\tau = \text{Const} \qquad (36)$$

[The expression for $\partial/\partial t(\psi\psi^*)$ is in the form of a divergence, and by Gauss' theorem this can be replaced by a surface integral, and for $R\to\infty$ this surface integral vanishes]

Putting $\rho = \psi^*\psi$ and

$$\vec{i} = \frac{\hbar}{2mi}\left(\psi^*\,\text{grad}\,\psi - \psi\,\text{grad}\,\psi^*\right) \qquad (38)$$

We notice, for future applications, that the differential equation above can be written as in the form of the Continuity equation

$$\frac{\partial\rho}{\partial t} + \text{div}\,\vec{i} = 0 \qquad (37)$$

When we expressly decide to count the time derivative of a real function as a new (second) function, we might say that <u>one single real function</u> contained in (37) <u>is not sufficient for the construction of a</u> any everywhere nowhere negative <u>probability</u>, out of waves of the form (24), which is whose integral over the volume <u>is a constant of the time</u>. On the contrary two real functions or one complex function and its conjugate are necessary.

[The real part of ψ viz $u = \frac{1}{2}(\psi+\psi^*)$ (similar the imaginary part) satisfies a differential equation which is not of the first order in time-derivatives but of

the second order. In fact it satisfies the "iterated" differential equation of the 2nd order

$$\left(-\frac{\hbar}{i}\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\Delta - E_0\right)\left(+\frac{\hbar}{i}\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\Delta - E_0\right) u = 0$$

or $$\left[\hbar^2\frac{\partial^2}{\partial t^2} + \left(\frac{\hbar^2}{2m}\Delta - E_0\right)^2\right] u = 0.$$

A quadratic expression built from u whose ~~too~~ volume integral is a time constant must contain not only u and its space derivatives but also its first time derivatives. This can be seen by forming $\frac{\partial}{\partial t}(u^2)$ by using the above differential equation. This also justifies the choice in (35) as the only possible one.]

The constants C_ρ in (35) can be included inside the ψ's so that we can write

$$W(x) = \sum_\rho \psi_\rho^* \psi_\rho = \sum_\rho |\psi_\rho|^2 \qquad (35)$$

as the most general assumption for the probability $W(x)$. We shall see later that many ψ-functions are necessary sometimes specially when one deals with particles having angular momentum. For the present however we will avoid this for the sake of ~~some~~ simplicity and operate with only one complex function, so that

$$W(x) = |\psi|^2 = \psi^*\psi \qquad (35')$$

with the normalisation condition

$$\int \psi^*\psi \, dV = 1 \qquad (36)$$

According to the continuity equation (37) we can interpret the expression (34) as the statistical current density or probability current. We interpret $\vec{i}(x)$ as the probability that the particle crosses a unit surface at right angles to the x-direction in unit time from the $-^{ve}$ to the $+^{ve}$ x direction.

In the case of a free particle whose momentum is constant, the probability

density $W(\vec{p})$ must itself (and not its integral) be a constant of the time. This probability density is given by

$$W(\vec{p}) = |\vec{A}(p)|^2 = A^* A = \varphi^* \varphi \qquad (39)$$

Alternatively we can write as definition

$$W(\vec{p}) = C(\vec{p}) \, |A(\vec{p})|^2$$

where $C(\vec{p})$ is a general positive function. On account of the completeness relation (28) which follows from (24) it is necessary that $C(\vec{p}) \equiv 1$ since from

$$\int W(x)\, dx = 1$$

must necessarily follow $\int W(p)\, dp = 1$

The means for the statistical description of any state of a ~~matter~~ free material particle is hereby completely given. Any such state is described by a wave packet $\psi(x,t)$ of the form (24) from which according to (39) there follows the "packet" $\varphi(\vec{p})$ in momentum space. These functions $\psi(x,t)$ and $\varphi(p)$ – often called "probability amplitudes" – are however, so far as their phase is concerned, not directly observable. On the contrary this is true of the probability densities $W(x,t)$ and $W(p)$. The complex wave functions themselves have therefore only a symbolic character and serve to determine the relation between $W(x,t)$ and $W(p)$.

From the general foundations developed we can draw some conclusions which can be directly compared with experimental results. In particular we can form mean values of certain functions of $\vec{x}$ or $\vec{p}$ and investigate their relationships or their time variations. For eg. we have

$$\overline{x_i} = \int x_i \, \psi^* \psi \, dV \; ; \; \overline{p_i} = \int p_i \, \varphi^* \varphi \, dp \qquad (40)$$

Also of interest are the ~~extensions~~ mean extensions of the packet which are given

by the "mean cross-sections"

$$\overline{(\Delta x_l)^2} = \int (x_l - \bar{x}_l)^2 \psi^* \psi \, dV \; ; \quad \overline{(\Delta p_l)^2} = \int (p_l - \bar{p}_l)^2 \varphi^* \varphi \, dp \tag{41}$$

The behaviour of the centre of a packet results from (26) and (27") and by partial integration as follows:-

$$\bar{x}_l = \frac{1}{\sqrt{(2\pi)^3}} \int x_l \psi^* dV \int \varphi(\vec{k}) e^{i(\vec{k}\vec{x})} dk$$

$$= \frac{1}{\sqrt{(2\pi)^3}} \int \psi^* dV \int \varphi(\vec{k}) \frac{1}{i} \frac{\partial}{\partial k_l} \left(e^{i(\vec{k}\vec{x})} \right) dk$$

$$= \frac{1}{\sqrt{(2\pi\hbar)^3}} \int \psi^* dV \int i\hbar \frac{\partial}{\partial p_l} [\varphi(\vec{p})] e^{\frac{i}{\hbar}(\vec{p},\vec{x})} dp \qquad \text{(by partial integration)}$$

$$= \frac{1}{\sqrt{(2\pi\hbar)^3}} \int i\hbar \frac{\partial}{\partial p_l} [\varphi(\vec{p})] dp \int \psi^* e^{\frac{i}{\hbar}(\vec{p},\vec{x})} dV \qquad \text{(changing the order of integration)}$$

$$= \int \varphi^*(\vec{p}) \, i\hbar \frac{\partial}{\partial p_l} [\varphi(p)] dp \qquad (\varphi^* \text{ \& } \psi^* \text{ being Fourier transforms})$$

Hence $$\bar{x}_l = \int \varphi^*(p) \cdot i\hbar \frac{\partial \varphi(p)}{\partial p_l} dp = \int \varphi^*(\vec{k}) \left(i \frac{\partial}{\partial k_l} \right) \varphi(\vec{k}) dk \tag{42}$$

or also $$\bar{x}_l = \int A^*(\vec{k}) \, e^{i\omega t} \left(i \frac{\partial}{\partial k_l} \right) \left[A(k) e^{-i\omega t} \right] dk \qquad \text{(using (25) \& (25*))}$$

& finally $$\bar{x}_l = \int A^* i \frac{\partial A}{\partial k_l} dk + t \int \frac{\partial \omega}{\partial k_l} A^* A \, dk \tag{43}$$

which signifies

$$\frac{d\bar{x}_l}{dt} = \overline{\left(\frac{\partial \omega}{\partial k_l} \right)} = \left(\overline{\frac{\partial E}{\partial p_l}} \right) = \bar{v}_l = \frac{\bar{p}_l}{m} \tag{44}$$

and represents the theorem of group-velocity. From the continuity equation it follows on the other hand by multiplication with x_l and partial integration

$$\frac{d\bar{x}_l}{dt} = \int \vec{v} \cdot \varrho \left(x_l \frac{\partial \dot{x}_l}{\partial x_l} + x_l \frac{\partial \dot{x}_m}{\partial x_m} + x_l \frac{\partial \dot{x}_n}{\partial x_n} \right) dV = \int j_l \, dV \qquad \text{(partial integration)}$$

$$i_l = \frac{\hbar}{2mi}\left(\psi^* \frac{\partial \psi}{\partial x_l} - \psi \frac{\partial \psi^*}{\partial x_l}\right)$$

and by partial integration $\int \psi^* \frac{\partial \psi}{\partial x_l} dV = \int \psi \frac{\partial \psi^*}{\partial x_l} dV.$

Hence, $\int i_l dV = \frac{\hbar}{mi} \int \psi^* \frac{\partial \psi}{\partial x_l} dV.$ Thus

$$\frac{d\overline{x_l}}{dt} = \int i_l dV = \frac{1}{m} \int \psi^* \left(\frac{\hbar}{i} \frac{\partial \psi}{\partial x_l}\right) dV \qquad (45)$$

Comparing with (44) we have

$$\overline{p_l} = \int \varphi^*(p)\, p_l\, \varphi(p)\, dp = \int \psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x_l} \psi\right) dV \qquad (46)$$

[Good exercise is to derive this directly just like $\overline{x_l}$]. The relations (42) and (46) can be further generalised. If $F(\vec{x})$ and $F(\vec{p})$ be rational integral functions of x_l and p_i respectively, one has

$$\overline{F(x_l)} = \int \psi^* F(x_l) \psi\, dV = \int \varphi^* F\left(i\hbar \frac{\partial}{\partial p_l}\right) \varphi\, dp \qquad (47)$$

$$\overline{F(p_l)} = \int \varphi^* F(p_l) \varphi\, dp = \int \psi^* F\left(\frac{\hbar}{i} \frac{\partial}{\partial x_l}\right) \psi\, dV \qquad (47')$$

as can be verified at once by partial integration and application of the Fourier Integral Theorem

[another good exercise to verify this statement]

we have accordingly

$$\overline{p_l^2} = \int \varphi^* p_l^2 \varphi\, dp = \int \psi^* \left(-\hbar^2 \frac{\partial^2 \psi}{\partial x_l^2}\right) dV = +\hbar^2 \int \frac{\partial \psi^*}{\partial x_l} \frac{\partial \psi}{\partial x_l} dV \text{ (integration by parts)}$$

$$\overline{x_l^2} = \int \psi^* x_l^2 \psi\, dp = \int \varphi^* \left(-\hbar^2 \frac{\partial^2 \varphi}{\partial p_l^2}\right) dp = +\hbar^2 \int \frac{\partial \varphi^*}{\partial p_l} \frac{\partial \varphi}{\partial p_l} dp.$$

To derive corresponding relations for $\overline{(\Delta x_l)^2}$ and $\overline{(\Delta p_l)^2}$ it is only necessary to

The simplest procedure is to make a transition to a new reference system given by the Galilean transformation

$$x' = x - x_0 - vt \; ; \quad t' = t$$

since we are here considering only the non-relativistic case. Also

$$p_x' = m(v_0 - v) = p_x - mv$$

$$E' = \tfrac{1}{2}m(v_0 - v)^2 = E - p_x v + \tfrac{1}{2}mv^2 .$$

In order to have the differential equation for φ' (see (26)) as

$$\frac{\hbar}{i}\frac{\partial \varphi'}{\partial t} = E'\varphi'$$

we put, $\varphi' = \varphi e^{-\frac{i}{\hbar}\left[\frac{1}{2}mv^2 - p_x v\right]t} \cdot e^{\frac{i}{\hbar}f}$

where f, which is independent of t, is so determined that the function

$$\psi' = \frac{1}{\sqrt{(2\pi\hbar)^3}} \int \varphi'(\vec{p}') e^{\frac{i}{\hbar}(\vec{p}'\vec{x}')} dp'$$

has the property $\psi'(\vec{x}') = \psi(\vec{x}')$

or $\psi'^*(\vec{x}')\psi'(\vec{x}') = \psi^*(\vec{x})\psi(\vec{x})$

In order that this condition may be satisfied

$$\int \varphi^*(p') e^{-\frac{i}{\hbar}(p'vt + f + p'x')} dp' \int \varphi(p') e^{\frac{i}{\hbar}(p'vt + f + p'x')} dp'$$

$$= \int \varphi^*(p) e^{-\frac{i}{\hbar}(px)} dp \int \varphi(p) e^{\frac{i}{\hbar}(px)} \cdot dp$$

ie it is sufficient to put (as can be seen by comparing with when the same region φ integrates)

$$pvt + f + px' = px$$

$$\text{ie} \quad p_x vt + f + p_x(x - x_0 - vt) = p_x x$$

$$\text{ie} \quad f = p_x x_0 .$$

We can therefore get expressions for $\varphi'(p')$ and $\psi'(x')$ as

$$\varphi'(\vec{p}') = \varphi(p)\, e^{\frac{i}{\hbar}\left[\frac{1}{2}mv^2t - p_x(x_0+vt)\right]} \tag{48}$$

$$\psi'(x') = \frac{1}{\sqrt{(2\pi\hbar)^3}} \int \varphi'(p')\, e^{\frac{i}{\hbar}(\vec{p}'\vec{x}')} \cdot dp'$$

$$= \frac{1}{\sqrt{(2\pi\hbar)^3}} \int \varphi(p)\, e^{-\frac{i}{\hbar}\left[\frac{1}{2}mv^2t - p_x x_0 - p_x vt - p_x' x'\right]} \cdot dp$$

$$\text{ie} \quad \psi'(x') = e^{-\frac{i}{\hbar}\left[mv(x-x_0) - \frac{1}{2}mv^2t\right]} \cdot \frac{1}{\sqrt{(2\pi\hbar)^3}} \int \varphi(p)\, e^{\frac{i}{\hbar}(p_x x)} \cdot dp$$

$$\text{ie} \quad \psi'(x') = \psi(x)\, e^{-\frac{i}{\hbar}\left[mv(x-x_0) - \frac{1}{2}mv^2t\right]} \tag{49}$$

$$\text{or} \quad \psi'(x',t') = \psi(x'+x_0+vt)\, e^{-\frac{i}{\hbar}\left[mvx' + \frac{1}{2}mv^2t'\right]} \tag{49'}$$

one can easily verify that these functions satisfy the differential equation

$$-\frac{\hbar}{i}\frac{\partial\psi'}{\partial t'} = \left(E_0 - \frac{\hbar^2}{2m}\Delta'\right)\psi'$$

For the current density $\vec{i}' = \frac{\hbar}{2mi}\left(\psi^{*\prime}\,\text{grad}\,\psi' - \psi'\,\text{grad}\,\psi^{*\prime}\right)$, we get by straightforward simplification

$$\vec{i}' = \vec{i} - \vec{v}\,\psi^*\psi \tag{50}$$

which can be very simply interpreted.

Since according to (43) the centre of the wave packet moves with constant velocity we can introduce a moving reference system k' moving with the centre which is therefore at rest in the new system. In this system

$$\overline{x} = 0, \quad \overline{p} = 0$$

$$\overline{x^2} = \overline{(x-\overline{x})^2} = \overline{(\Delta x)^2}\,; \quad \overline{p^2} = \overline{(p-\overline{p})^2} = \overline{(\Delta p)^2}$$

To simplify the writing (like $\overline{x_i'} = 0$, etc) we consider the one dimensional case only

$$\overline{p^2} = \int p^2 \varphi^* \varphi \, dp = \hbar^2 \int \frac{\partial \psi^*}{\partial x} \cdot \frac{\partial \psi}{\partial x} \, dV$$

and by using (49) this can be shown to be independent of time. On the other hand,

$$\overline{x^2} = \int x^2 \psi^* \psi \, dV = \hbar^2 \int \frac{\partial \varphi^*}{\partial p} \cdot \frac{\partial \varphi}{\partial p} \, dp$$

From (48), $\frac{\partial \varphi^{*\prime}}{\partial p} = \frac{\partial \varphi^*}{\partial p} e^{+\frac{i}{\hbar}[\,]} + \varphi^* e^{+\frac{i}{\hbar}[\,]} \cdot \frac{i}{\hbar}(-x_0 - vt)$

$$\frac{\partial \varphi'}{\partial p} = \frac{\partial \varphi}{\partial p} e^{-\frac{i}{\hbar}[\,]} + \varphi e^{-\frac{i}{\hbar}[\,]} \cdot \frac{i}{\hbar}(x_0 + vt)$$

Hence $\frac{\partial \varphi^{*\prime}}{\partial p} \cdot \frac{\partial \varphi'}{\partial p} = \frac{\partial \varphi^*}{\partial p} \frac{\partial \varphi}{\partial p} + \frac{\partial \varphi^*}{\partial p} \cdot \frac{i}{\hbar}(x_0 + vt)\varphi - \varphi^* \frac{i}{\hbar}(x_0 + vt)\frac{\partial \varphi}{\partial p} + \varphi^* \varphi \frac{i^2}{\hbar^2}(x_0 + vt)^2$

Hence $\overline{x^2} = \hbar^2 \int \frac{\partial \varphi^*}{\partial p} \frac{\partial \varphi}{\partial p} dp + i\hbar t \int v \left(\frac{\partial \varphi^*}{\partial p} \varphi - \varphi^* \frac{\partial \varphi}{\partial p} \right) dp + t^2 \int v^2 \varphi^* \varphi \, dp$

$$+ i\hbar \int x_0 \left(\frac{\partial \varphi^*}{\partial p} \varphi - \varphi^* \frac{\partial \varphi}{\partial p} \right) dp + \int (x_0^2 + 2 x_0 vt) \varphi^* \varphi \, dp.$$

with $x_0 = 0$, this reduces, after taking (25) into consideration, also with $v = \partial E / \partial p$,

$$\overline{x^2} = \hbar^2 \int \frac{\partial A^*}{\partial p} \frac{\partial A}{\partial p} dp + i\hbar t \int \frac{\partial E}{\partial p} \left(A^* \frac{\partial A}{\partial p} - A \frac{\partial A^*}{\partial p} \right) dp + t^2 \int \left(\frac{\partial E}{\partial p} \right)^2 A^* A \, dp \qquad (51)$$

or $$\overline{x^2} = \hbar^2 \int \frac{\partial A^*}{\partial p} \cdot \frac{\partial A}{\partial p} dp + \frac{i\hbar t}{m} \int p \left(A^* \frac{\partial A}{\partial p} - A \frac{\partial A^*}{\partial p} \right) dp + \frac{t^2}{m^2} \overline{p^2} \qquad (51')$$

The mean square scatter cross-section of an arbitrary wave packet along any coordinate direction in the case of a force free particle a quadratic function of the time. After passing through a minimum it becomes arbitrarily large both before and after. It is also simple to write (51') from momentum- coordinate space. Let ψ_0 be the value of ψ for $t = 0$, $\overline{(x^2)}_0 = \int x^2 \psi_0^* \psi_0 \, dV$ the value of $\overline{x^2}$ for $t = 0$, $\vec{i}_0 = \frac{\hbar}{2mi} (\psi_0^* \cdot \operatorname{grad} \psi_0 - \psi_0 \operatorname{grad} \psi_0^*)$ the value of $\vec{i}$ at time $t = 0$, one derives

$$\overline{x^2} = \overline{(x^2)}_0 + 2t \int (xi) \, dV + \frac{t^2}{m^2} \overline{p^2} \qquad (52')$$

by transforming the terms in (51') from A's (or Φ's) to ψ's. ~~(Thus does too.~~ Thus

$$\hbar^2 \int \frac{\partial A_0^*}{\partial p} \frac{\partial A_0}{\partial p}\, dp = \int x^2 \psi_0^* \psi_0\, dV = \overline{(x_0^2)}_0$$

$$\frac{\hbar i}{m} \int p \left(A_0^* \frac{\partial A_0}{\partial p} - A_0 \frac{\partial A_0^*}{\partial p} \right) dp = \frac{\hbar i}{m} \int x \left(\psi_0^* \frac{\partial \psi_0}{\partial x} - \psi_0 \frac{\partial \psi_0^*}{\partial x} \right) dV = \frac{\hbar}{m} \int (\rho i)\, dV .$$

Writing (52') in the non-accented system (with $\rho = \psi^* \psi$) + using (50)

$$\overline{\Delta x^2} = \overline{(\Delta x^2)}_0 + 2t \int (x - \bar{x}) \left(i - \frac{\rho}{m} p \right) dV + \frac{t^2}{m^2} \overline{(\Delta p)^2} \qquad (52)$$

This result contains nothing which is characteristic for the quantum theory for in case of a system of forcefree moving particles with density ρ and current density $\vec{i}$ and also with the mean square $\overline{(\Delta p_x^2)}$ of the momentum distributed we get the same result classically. But it reminds one that the continuity of $\bar{x}$ and Δx as a function of x (for arbitrarily small $\overline{(\Delta x)^2_0}$ is essential for the repeatability of measurement of position. In the three dimensional case we can also deduce, for the time variation of the mean values $\overline{\Delta x_l \Delta x_m}$ of the product of two coordinates, the analogous quadratic form

$$\overline{\Delta x_l \Delta x_m} = \overline{(\Delta x_l \Delta x_m)}_0 + t \int \left[(x_l - \bar{x}_l)\left(i_m - \frac{\rho}{m} p_m \right) + (x_m - \bar{x}_m)\left(i_l - \frac{\rho}{m} p_l \right) \right] dV + \frac{t^2}{m^2} \overline{\Delta p_l \Delta p_m} \qquad (53)$$

What is characteristic for the quantum theory is however the relation existing between $\overline{(\Delta x)^2}$ and $\overline{(\Delta p)^2}$ which corresponds to the uncertainty relation, because both the expressions cannot be simultaneously made arbitrarily small. This is seen at once by considering the inequality

$$D = \left| \frac{x}{2\sqrt{\overline{x^2}}} \psi + \frac{\partial \psi}{\partial x} \right|^2 \geq 0 .$$

$$D = \frac{x^2}{4\overline{x^2}} \psi \psi^* + \frac{x}{2\overline{x^2}} \left(\psi \frac{\partial \psi^*}{\partial x} + \psi^* \frac{\partial \psi}{\partial x} \right) + \frac{\partial \psi}{\partial x} \frac{\partial \psi^*}{\partial x}$$

$$= \frac{1}{4}\left(\frac{x}{\overline{x^2}}\right)^2 \psi\psi^* + \frac{1}{2}\frac{\partial}{\partial x}\left(\frac{x}{\overline{x^2}}\psi\psi^*\right) - \frac{1}{2}\cdot\frac{1}{\overline{x^2}}\psi\psi^* + \frac{\partial\psi}{\partial x}\frac{\partial\psi^*}{\partial x}$$

$$= \frac{1}{4}\cdot\frac{1}{(\overline{x^2})^2}\cdot\left[x^2 - 2\overline{x^2}\right]\psi\psi^* + \frac{1}{2}\frac{\partial}{\partial x}\left(\frac{x}{\overline{x^2}}\psi\psi^*\right) + \frac{\partial\psi}{\partial x}\frac{\partial\psi^*}{\partial x}$$

Integrating $\int \frac{\partial}{\partial x}\left(\frac{x}{\overline{x^2}}\psi\psi^*\right) dV = 0$

$$\int \frac{1}{4}\cdot\frac{1}{(\overline{x^2})^2}\left[x^2 - 2\overline{x^2}\right]\psi\psi^* dV = \frac{1}{4}\cdot\frac{1}{(\overline{x^2})^2}\left[\overline{x^2} - 2\overline{x^2}\right] = -\frac{1}{4}\cdot\frac{1}{\overline{x^2}}$$

$$\int \frac{\partial\psi}{\partial x}\frac{\partial\psi^*}{\partial x} dV = \frac{1}{\hbar^2}\overline{p^2}$$

$\therefore \int D\, dV \geq 0$ gives

$$\overline{p^2}\,\overline{x^2} = \overline{(\Delta p)^2}\,\overline{(\Delta x)^2} \geq \frac{\hbar^2}{4} \qquad (54)$$

This is the quantitatively sharpened form of the uncertainty relation. The equality in (54) results only when

$$\frac{1}{\lambda}\frac{x}{\overline{x^2}}\psi + \frac{\partial\psi}{\partial x} = 0$$

$$\text{i.e.} \quad \psi = C e^{-\frac{1}{4}\frac{x^2}{\overline{x^2}}} \qquad (55)$$

~~Whilst $\overline{\Delta p_i^2}$ is a time-constant, $\overline{\Delta x_i^2}$ varies with time~~

In general when all the coordinates are considered

$$\psi = C' e^{-\frac{1}{4}\left(\frac{x_1^2}{\overline{x_1^2}} + \frac{x_2^2}{\overline{x_2^2}} + \frac{x_3^2}{\overline{x_3^2}}\right)} \qquad (55')$$

While $\overline{\Delta p_i^2}$ is a time-constant, $\overline{\Delta x_i^2}$ varies with the time. If the minimum of the product $\overline{(\Delta p_i)^2}\overline{(\Delta x_i)^2}$ is reached when $t = 0$, then the linear term in t in (52) must be zero and then for later or earlier times we get greater values for the product. In any case it is impossible for subsequent measurements to be more and more refined

but never below the minimum.

The momentum function $\varphi(p)$ which corresponds to this minimum is because of the complete symmetry of the minimum problem in relation to p_x and x equally the Gaussian error-function

$$\varphi(p) = C e^{-\frac{1}{4}\cdot\frac{p_x^2}{(\Delta p_x)^2}} \tag{56}$$

$$\text{and} \qquad \varphi(p) = C e^{-\frac{1}{4}\left[\frac{p_1^2}{(\Delta p_1)^2}+\frac{p_2^2}{(\Delta p_2)^2}+\frac{p_3^2}{(\Delta p_3)^2}\right]} \tag{56'}$$

This can also be immediately verified by calculation with the aid of (24").

Finally we shall describe a method for the solution of the time-dependent equation (29) when the space function ψ_0 for $t=0$ is specified. According to the general method of partial differential equations one has to find a "Grundlösung" $U(x_i,t)$ which has the property that for $t=0$ it is singular in such a way that for every finite domain of integration

$$\lim_{t\to 0}\int_{(V)} U\,dV = \begin{cases} 1, & \text{when the zero point lies in } V \\ 0, & \text{when the zero point lies outside } V \end{cases} \tag{57}$$

on account of the linear character of the differential equation the required solution is

$$\left.\begin{aligned}\psi(x_i,t) &= -\int U(\bar{x}_i - x_i, t)\,\psi(\bar{x}_i;0)\,dV \\ &= \int U(\bar{x}_i;t)\,\psi(x_i+\bar{x}_i;0)\,dV\end{aligned}\right\} \tag{58}$$

To find U for the force-free case of non-relativistic wave mechanics it is convenient to recognise its formal analogy with the differential equation

$$\frac{\partial\psi}{\partial} = \frac{ih}{} \Delta\psi \tag{59}$$

of heat conduction or diffusion. (We put here $E_0 = 0$ for simplicity since we can arrive at this case by separation of $e^{-i/\hbar E_0 t}$ from the ψ-function). We have here to substitute, however, for the heat conduction coefficient an imaginary number. Our fundamental solution then corresponds to a "heat source" solution of the heat conduction equation, and in the one-dimensional case it reads as

$$U(x,t) = \frac{C}{\sqrt{t}} e^{-\frac{im}{2\hbar}\cdot\frac{x^2}{t}}$$

It is easily to verify at once that this function satisfies the differential equation

$$\frac{\partial \psi}{\partial t} = \frac{i\hbar}{2m}\cdot\frac{\partial^2 \psi}{\partial x^2}.$$

And we have

$$\int_{x_1}^{x_2} U(x,t)\,dx = C\sqrt{\frac{2\hbar}{m}} \int_{\sqrt{\frac{m}{2\hbar}}\cdot\frac{x_1}{\sqrt{t}}}^{\sqrt{m/2\hbar}\cdot\frac{x_2}{\sqrt{t}}} e^{i\xi^2}\,d\xi$$

Now for, $\lim a \to +\infty$; $\lim b \to +\infty$, $\lim \int_a^b e^{i\xi^2} d\xi = 0$

and, $\lim a \to -\infty$; $\lim b \to +\infty$; $\lim \int_a^b e^{i\xi^2} d\xi = \int_{-\infty}^{+\infty} e^{i\xi^2} d\xi = \sqrt{\pi}\, e^{i\pi/4}$

and accordingly, as required in (57)

$$\lim_{t\to 0} \int_{x_1}^{x_2} U\,dx = \begin{cases} 0 & \text{when the origin } x=0 \text{ lies } \begin{cases} \text{outside} \\ \text{inside} \end{cases} \text{ the interval } (x_1, x_2) \\ 1 \end{cases}$$

when the constant C is chosen such that $C = e^{-i\pi/4}\sqrt{(m/2\pi\hbar)}$. Thus we have finally

$$U(x,t) = e^{-i\pi/4}\sqrt{\left(\frac{m}{2\pi\hbar}\right)}\,\frac{1}{\sqrt{t}}\,e^{\frac{im}{2\hbar}\frac{x^2}{t}} \qquad (60)$$

For the three dimensional case we obtain at once by forming the factor product

$$U(x_1, x_2, x_3; t) = U(x_1, t) \cdot U(x_2, t)\, U(x_3, t)$$

$$= e^{-\frac{3\pi i}{4}} \left(\frac{m}{2\pi\hbar}\right)^{3/2} \frac{1}{t^{3/2}}\, e^{\frac{im}{2\hbar}\frac{x_1^2 + x_2^2 + x_3^2}{t}} \qquad (61)$$

Substituting this in (58) one obtains the general solution of the wave equation. The investigation of U enables us to find its decomposition into Fourier components according to (24) and (27).

(4) Wave function of a particle under the action of forces: The description of the state of particles subject to forces is obtained by generalising the statistical notions and rules used in the case of free particles. Obviously these notions and laws must be not be self-contradictory and must contain the classical particle mechanics as a limiting case. Apart from these general conditions, only practical applicability can distinguish between the several assumptions. We can formulate these assumptions in the following way for the case of a single particle, ignoring the relativistic corrections:-

(i) The probability of finding the space coordinate x_i between x_i and $x_i + dx_i$ at a determined time t is a valid conception. It is again given by

$$W(x_1, x_2 x_3; t)\, dx_1\, dx_2 dx_3 = \psi^* \psi\, dx_1\, dx_2\, dx_3 \qquad (36)$$

wherein ψ denotes a non-observable complex wave function and ψ^* its conjugate complex function. ψ is also normalised according to

$$\int \psi \psi^* dV = 1$$

This assumption is quite obvious because the determination of position can be achieved can be in such a short time that the presence of the forces does not play any part. From (36) follows for the time-variation of ψ the condition

$$\frac{d}{dt}\int \psi\psi^* dV = 0$$

this can only be satisfied for every instant of time if $\partial\psi/\partial t$ and $\partial\psi^*/\partial t$ are determined simultaneously also with ψ and ψ^*.

(ii) When we put

$$-\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = \underline{\underline{H}}\,\psi \tag{62}$$

$\underline{\underline{H}}$ shall be a linear and not a general operator. As already mentioned this is equivalent to the setting up of a correspondence of a new function $\underline{\underline{H}}\psi$ to a function ψ with the property that for an arbitrary constant, which may also be complex, one has

$$\underline{\underline{H}}(c\psi) = c\,\underline{\underline{H}}(\psi),$$

and for two arbitrary functions ψ_1 and ψ_2

$$\underline{\underline{H}}(\psi_1+\psi_2) = \underline{\underline{H}}(\psi_1) + \underline{\underline{H}}(\psi_2)$$

[From these two properties it follows besides that $\underline{\underline{H}}(\psi)$ does not explicitly depend on ψ^*.]

The condition of linearity of the operator $\underline{\underline{H}}$ can be considered a generalisation of the Superposition principle, for as we have seen in the force free case, ~~has gives directly~~ the principles of the wave theory give this expression directly. This principle is essential for a contradiction-free formulation of the notion of measurement as well as for the quantum-theoretic description of the coupling of the system with the measuring apparatus.

Since the constancy of $\int\psi\psi^* dV$ is satisfied according to (62) $\underline{\underline{H}}$ must have the property

$$\int\left[\psi^*\underline{\underline{H}}\psi - \psi(\underline{\underline{H}}\psi)^*\right]dV = 0 \tag{63}$$

Here, as usual, ψ^* satisfies the wave equation

$$+\frac{\hbar}{i}\frac{\partial\psi^*}{\partial t} = (H\psi)^* \tag{62*}$$

This (cf (63)) must be valid for all regular functions which vanish sufficiently rapidly at infinity. An operator $\underline{\underline{H}}$, which possesses this property, is called hermitian. On account of the linearity of $\underline{\underline{H}}$ it follows from (63) that for two arbitrary functions

$$\int [\psi_1^* \underline{\underline{H}} \psi_2 - \psi_2 (\underline{\underline{H}} \psi_1)^*] \, dV = 0$$

[one can derive a continuity eqn $\frac{\partial (\psi_1^* \psi_2)}{\partial t} + \operatorname{div} \vec{i}_{12} = 0$ and show this equation to be true]

(iii) The relations (24"), (27) which connect ψ with the "amplitude" $\varphi(p)$ determining the probability $W(p_i, t)\, dp_1 dp_2 dp_3$ according to (39) are also valid in this case; only the probability is no longer a constant. This connection was first given by P. Jordan.

[It might be remarked here that from (63) alone the linearity of $\underline{\underline{H}}$ does not follow. For eg. consider the non-linear operator $\underline{\underline{H}}(\psi) = i \psi \psi^* \frac{\partial \psi}{\partial x}$ (so that $(H\psi)^* = -i \psi^* \psi \frac{\partial \psi^*}{\partial x}$); for this the property (63) is satisfied for

$$\psi^* \underline{\underline{H}} \psi - \psi (\underline{\underline{H}} \psi)^* = i \psi \psi^* \frac{\partial \psi}{\partial x} + i \psi^2 \psi^* \frac{\partial \psi^*}{\partial x} = \frac{1}{2} i \frac{\partial}{\partial x} (\psi^2 \psi^{*2})$$

It is accordingly necessary to formulate the superposition principle as a new assumption].

From the standpoint of non-relativistic mechanics the unique one way of finding the operator $\underline{\underline{H}}$ for a definite system corresponds, according to Bohr's correspondence principle, to the comparison of the properties of the general solution of (62) with the properties of the mechanical orbits of the same system in the classical limiting case. Between several such possibilities for $\underline{\underline{H}}$ satisfying the correspondence principle only experiment can decide.

As the simplest example let us consider a particle in an external field with a potential function $V(x, x_2, x_3)$. The classical Hamilton function

reads

$$H(p_i, x_i) = \sum_i \frac{p_i^2}{2m} + V(x_i)$$

In view of the fact that according to (47') the expectation value of p_i^2 is given by

$$\overline{p_i^2} = \int p_i^2 |\varphi(p)|^2 dp = -\hbar^2 \int \psi^* \frac{\partial^2 \psi}{\partial x_i^2} dV$$

it is natural to assume with Schrödinger the wave equation in the form

$$-\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \Delta \psi + V\psi \qquad (64)$$

we shall derive from this some conclusions about mean values which are analogous to those derived in the previous article. First according to (64) follows the Continuity Equation

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \vec{i} = 0$$

with $\rho = \psi^* \psi$ and the original expression (38)

$$i_k = \frac{\hbar}{2mi} \left(\psi^* \frac{\partial \psi}{\partial x_k} - \psi \frac{\partial \psi^*}{\partial x_k} \right)$$

for the current-density; because in the calculation of $\partial \rho / \partial t$ the terms in $V\psi$ cancel themselves.

From this it follows further as in (44), (45) and (46) the relations

$$\bar{x}_k = \int x_k \psi^* \psi \, dV \; ; \; \bar{p}_k = \int p_k \varphi^* \varphi \, dp = \int \psi^* \left(\frac{\hbar}{i} \frac{\partial \psi}{\partial x} \right) dV$$

$$\frac{d\bar{x}_k}{dt} = \int i_k \, dV = \frac{1}{m} \bar{p}_k = \overline{\left(\frac{\partial H}{\partial p_k} \right)}$$

we have however to calculate anew the variation $d\bar{p}_k/dt$ of $\bar{p}_k$ with the time since this always vanishes in the force-free case; but this is not true in the present case. For this purpose let us form first

$$m \cdot \frac{\partial \dot{x}_k}{\partial t} = \frac{1}{2} \left(\underline{\underline{H}} \psi^* \right) \frac{\partial \psi}{\partial x_k} - \psi^* \frac{\partial}{\partial x_k} \left(\underline{\underline{H}} \psi \right) + \left(\underline{\underline{H}} \psi \right) \frac{\partial \psi^*}{\partial x_k} - \psi \frac{\partial}{\partial x_k} \left(\underline{\underline{H}} \psi \right)^*$$

$$= \frac{\hbar^2}{4m}\left[-(\Delta\psi^*)\frac{\partial\psi}{\partial x_k} + \psi^*\frac{\partial}{\partial x_k}(\Delta\psi) - (\Delta\psi)\frac{\partial\psi^*}{\partial x_k} + \psi\frac{\partial}{\partial x_k}(\Delta\psi^*)\right]$$

$$+\frac{1}{2}\left[V\psi^*\frac{\partial\psi}{\partial x_k} - \psi^*\frac{\partial}{\partial x_k}(V\psi) + V\psi\frac{\partial\psi^*}{\partial x_k} - \psi\frac{\partial}{\partial x_k}(V\psi^*)\right]$$

The second bracket simplifies immediately to $-\frac{\partial V}{\partial x_k}\psi^*\psi$. The first bracket is to be rewritten as follows: For two arbitrary functions u, v one has

$$v\Delta u - u\Delta v = \sum_l \frac{\partial}{\partial x_l}\left(v\frac{\partial u}{\partial x_l} - u\frac{\partial v}{\partial x_l}\right).$$

Putting here once $v = \psi^*$, $u = \frac{\partial\psi}{\partial x_k}$, another time $v = \psi$, $u = \frac{\partial\psi^*}{\partial x_k}$, and introducing the force $K_l = -\frac{\partial V}{\partial x_l} = -\frac{\partial H}{\partial x_l}$, we have

$$m\frac{\partial i_k}{\partial t} = -\sum\frac{\partial T_{kl}}{\partial x_l} + K_k\psi^*\psi \qquad (65)$$

with

$$T_{kl} = \frac{\hbar^2}{4m}\left[-\psi^*\frac{\partial^2\psi}{\partial x_k\partial x_l} - \psi\frac{\partial^2\psi^*}{\partial x_k\partial x_l} + \frac{\partial\psi}{\partial x_k}\frac{\partial\psi^*}{\partial x_l} + \frac{\partial\psi^*}{\partial x_k}\frac{\partial\psi}{\partial x_l}\right] \qquad (66)$$

The tensor T_{kl} which satisfies the usual symmetry condition

$$T_{kl} = T_{lk} \qquad (66')$$

can be designated as the ~~tensor~~ stress-tensor. From it we obtain at once

$$\frac{d\bar{p}_k}{dt} = m\frac{d^2\bar{x}_k}{dt^2} = m\int\frac{\partial i_k}{\partial t}dV = \int K_k\psi^*\psi\,dV = \overline{K_k} = -\left(\overline{\frac{\partial V}{\partial x_k}}\right) = -\left(\frac{\overline{\partial H}}{\partial x_k}\right)$$

$$- \quad .(67)$$

which denotes that the time derivative of the mean value of p_k is equal to the mean value of the force on the wave packet. This last is in general different from the force at the point of the mean centre $\bar{x}_k$ of the

wave-packet. When the wave packet is chosen, in consonance with the uncertainty relation $\Delta p_k \Delta x_k \sim \hbar$, such that the force varies only slightly in the region of the packet we obtain a property of the packet similar to a classical particle that satisfied by the orbit of the equations of motion (Cf. § 12)

$$m \frac{d^2 x_k}{dt^2} = - \frac{\partial V}{\partial x_k}.$$

Another deduction from (65) concerns the Virial theorem. Multiplying (65) by x_k and integrating by parts, we have

$$m \frac{\partial}{\partial t} \int x_k i_k \, dV = + \int T_{kk} \, dV - \int x_k \frac{\partial V}{\partial x_k} \psi^* \psi \, dV$$

on account of (66) the first integral on the right hand side gives on integration by parts $\frac{\hbar^2}{m} \int \frac{\partial \psi^*}{\partial x_k} \frac{\partial \psi}{\partial x_k} \, dV = \frac{\overline{p_k^2}}{m}$, and accordingly

$$m \frac{\partial}{\partial t} \int x_k i_k \, dV = \frac{\overline{p_k^2}}{m} - \overline{\left(x_k \frac{\partial V}{\partial x_k} \right)} \qquad (68)$$

Summing over the index k, we obtain the analogue of the Virial theorem.

Finally we might consider the time-variation of the cross-section of a wave-packet given by

$$\overline{(\Delta x_k)^2} = \int (x_k - \bar{x}_k)^2 \psi^* \psi \, dV \qquad (69)$$

Now, on account of the action of the forces it is in general no longer possible to calculate give the variation of $\overline{(\Delta x_k)^2}$ for finite time; on the other hand we can obtain instead the first and second differential coefficients of $\overline{(\Delta x_k)^2}$ with respect to time. Since $\int (x_k - \bar{x}_k) \psi^* \psi \, dV = 0$ we obtain first of all

$$\frac{d}{dt}\overline{(\Delta x_k)^2} = \int (x_k - \bar{x}_k)^2 \frac{\partial}{\partial t}(\psi^*\psi)\, dV$$

$$\left[\frac{d}{dt}\overline{(\Delta x_k)^2} = \int \frac{\partial}{\partial t}(x_k - \bar{x}_k)^2 \psi^*\psi\, dV + \int (x_k - \bar{x}_k)^2 \frac{\partial}{\partial t}(\psi^*\psi)\, dV \right.$$

$$\text{and the first integral} = 2\int (x_k - \bar{x}_k)\frac{\partial}{\partial t}(x_k - \bar{x}_k)\psi^*\psi\, dV$$

$$= -2\frac{\bar{p}_k}{m}\int (x_k - \bar{x}_k)\psi^*\psi\, dV = 0 \left.\right]$$

and applying the continuity equation and partial integration, this gives

$$\frac{d}{dt}\overline{(\Delta x_k)^2} = 2\int (x_k - \bar{x}_k) i_k\, dV \qquad (70)$$

$$\left[-\int (x_k - \bar{x}_k)^2 \operatorname{div}\vec{i}\cdot dV = -\iiint (x_k - \bar{x}_k)^2 \left(\frac{\partial i_k}{\partial x_k} + \frac{\partial i_l}{\partial x_l} + \frac{\partial i_m}{\partial x_m} \right) dx_k\, dx_l\, dx_m = 2\int (x_k - \bar{x}_k) i_k\, dV \right.$$

by partial integration $\left.\right]$

and $$\frac{1}{2}\frac{d^2}{dt^2}\overline{(\Delta x_k)^2} = \int \frac{\partial}{\partial t}\{(x_k - \bar{x}_k) i_k\}\, dV = \int (x_k - \bar{x}_k)\frac{\partial i_k}{\partial t}\, dV - \frac{d\bar{x}_k}{dt}\int i_k\, dV$$

and on account of the fact that

$$\frac{d\bar{x}_k}{dt} = \int i_k\, dV = \frac{\bar{p}_k}{m} \quad \text{this gives}$$

$$\frac{1}{2}\frac{d^2}{dt^2}\overline{(\Delta x_k)^2} = \int (x_k - \bar{x}_k)\frac{\partial i_k}{\partial t}\, dV - \left(\int i_k\, dV\right)^2$$

$$\left[\text{From (65)} \quad m\int (x_k - \bar{x}_k)\frac{\partial i_k}{\partial t}\, dV = \int (x_k - \bar{x}_k)\sum_l \frac{\partial T_{kl}}{\partial x_l}\, dV + \int (x_k - \bar{x}_k) K_k \psi^*\psi\, dV \right.$$

$$\int (x_k - \bar{x}_k)\frac{\partial i_k}{\partial t} = \frac{\partial}{\partial t}\int x_k i_k\, dV - \bar{x}_k \int \frac{\partial i_k}{\partial t}\, dV$$

$$= \frac{\overline{p_k^2}}{m^2} + \frac{1}{m}\overline{(x_k K_k)} - \frac{1}{m}\bar{x}_k \bar{K}_k \qquad \text{using (68) and (67)}$$

and $$\overline{(\Delta x_k \Delta K_k)} = \int (x_k - \bar{x}_k)(K_k - \bar{K}_k)\psi^*\psi\, dV = \overline{(x_k K_k)} - 2\bar{x}_k \bar{K}_k + \bar{x}_k \bar{K}_k$$

and hence finally

$$\frac{1}{2} m \frac{d^2}{dt^2}\overline{(\Delta x_k)^2} = \frac{\overline{p_k^2} - \overline{(p_k)}^2}{m} + \overline{(\Delta x_k \Delta K_k)}$$

or

$$\frac{1}{2} m \frac{d^2}{dt^2}\overline{(\Delta x_k)^2} = \frac{\overline{(p_k - \bar{p}_k)^2}}{m} + \overline{(\Delta x_k \Delta K_k)} \qquad (71)$$

Relations (70) and (71) represent the natural generalisations of (52).

Before proceeding to consider the question of interaction of several particles, we shall find what modifications are necessary for the wave equation due to the presence of an external magnetic field. If Φ_k be the components of the vector-potential, e the charge of the particle and c the velocity of light the magnetic field strength is given by

$$H_{kl} = \frac{\partial \Phi_l}{\partial x_k} - \frac{\partial \Phi_k}{\partial x_l} \qquad (72)$$

and in the case where Φ_k depends explicitly on the time the electric field strength is

$$E_k = -\frac{1}{c}\frac{\partial \Phi_k}{\partial t} \qquad (73)$$

and the force is

$$\left.\begin{aligned} K_k &= -\frac{\partial V}{\partial x_k} + \frac{e}{m}\left(E_k + \frac{1}{c}\sum_l H_{kl}\dot{x}_l\right) \\ &= -\frac{\partial V}{\partial x_k} + \frac{e}{c}\left[-\frac{\partial \Phi_k}{\partial t} + \sum_l \left(\frac{\partial \Phi_l}{\partial x_k} - \frac{\partial \Phi_k}{\partial x_l}\right)\dot{x}_l\right] \end{aligned}\right\} \qquad (74)$$

$$\left[\sum_l H_{1l}\dot{x}_l = \dot{x}_2 H_{12} + \dot{x}_3 H_{13} = \dot{x}_2 H_{12} - \dot{x}_3 H_{31} = \left[\vec{\dot{x}} \times \vec{H}\right]_1\right]$$

As is well-known the mechanical equations of motion

$$m\frac{d^2 x_k}{dt^2} = K_k$$

with the above value for the force can be written in the canonical form

$$\frac{dx_k}{dt} = \frac{\partial H}{\partial p_k}, \quad \frac{dp_k}{dt} = \frac{\partial H}{\partial x_k}$$

when $\underline{\underline{H}} = \sum_k \frac{1}{2m}\left(p_k - \frac{e}{c}\Phi_k\right)^2 + V(x)$. (75)

we then have, $\dot{x}_k = \frac{1}{m}\left(p_k - \frac{e}{c}\Phi_k\right)$; $p_k = m\dot{x}_k + \frac{e}{c}\Phi_k$ (75')

[Starting with (75') it can be shown directly that $\frac{dp_x}{dt} = -\frac{\partial H}{\partial x_k}$ is equivalent to $m\ddot{x}_k = K_k$]

as the relation between momentum and velocity.

The fact that the classical Hamiltonian (75) follows from the corresponding one in which no magnetic field is present by the substitution of p_k by $p_k - \frac{e}{c}\Phi_k$ suggests that the ~~corresponding~~ wave equation corresponding to (64) is to be obtained by substituting $\frac{\hbar}{i}\frac{\partial}{\partial x_k} - \frac{e}{c}\Phi_k$ for $\frac{\hbar}{i}\frac{\partial}{\partial x_k}$. We then obtain in place of (64) the more general equation

$$-\frac{\hbar}{i}\frac{\partial \psi}{\partial t} = \frac{1}{2m}\sum_k\left(\frac{\hbar}{i}\frac{\partial}{\partial x_k} - \frac{e}{c}\Phi_k\right)\left(\frac{\hbar}{i}\frac{\partial}{\partial x_k} - \frac{e}{c}\Phi_k\right)\psi + V\psi = 0, \qquad (76)$$

which can be also be written as

$$-\frac{\hbar}{i}\frac{\partial \psi}{\partial t} = \frac{1}{2m}\sum_k\left[-\hbar^2\Delta\psi - \frac{\hbar e}{ic}\frac{\partial}{\partial x_k}(\Phi_k\psi) - \frac{\hbar e}{ic}\Phi_k\frac{\partial \psi}{\partial x_k} + \frac{e^2}{c^2}\Phi_k^2\psi\right] + V\psi = 0. \qquad (76')$$

The justification for this expression lies in the fact that we can derive from it theorems on mean values of p_k, x_k and the total current $\bar{i}_k = \int i_k\, dv$ and its time-derivative which are analogous to the corresponding equations of motion of classical mechanics.

First we notice that the continuity equation

$$\frac{\partial}{\partial t}(\psi^*\psi) + \operatorname{div}\bar{i}^* = 0 \qquad (37)$$

is valid from which it follows at once that $\underline{\underline{H}}$ is in fact a Hermitian operator

[From continuity eqn follows $\frac{d}{dt}\int \rho\, dV = 0$, and this along with assumption of linearity of $\underline{\underline{H}}$ leads to the Hermiticity]

For the current however we have the next expression

$$i_k = \frac{1}{2m}\left[\psi^*\left(\frac{\hbar}{i}\frac{\partial}{\partial x_k} - \frac{e}{c}\bar{\Phi}_k\right)\psi - \psi\left(\frac{\hbar}{i}\frac{\partial}{\partial x_k} + \frac{e}{c}\bar{\Phi}_k\right)\psi^*\right] \tag{77}$$

or

$$i_k = \frac{\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial x_k} - \psi\frac{\partial\psi^*}{\partial x_k}\right) - \frac{e}{mc}\bar{\Phi}_k\psi^*\psi \tag{77'}$$

Forming

$$\bar{p}_k = \int p_k \varphi^*\varphi\, d\beta = \int \psi^*\frac{\hbar}{i}\frac{\partial\psi}{\partial x_k}\, dV$$

and

$$\frac{d\bar{x}_k}{dt} = \frac{\partial}{\partial t}\int x_k \psi^*\psi\, dV = \int i_k\, dV$$

we find,

$$\frac{d\bar{x}_k}{dt} = \frac{1}{m}\left(\bar{p}_k - \frac{e}{c}\bar{\Phi}_k\right), \text{ (using (77'))} \tag{75''}$$

which is analogous to (75').

Further in analogy with (65) and (66)

$$m\frac{\partial i_k}{\partial t} = -\sum_l \frac{\partial T_{kl}}{\partial x_l} + \left(-\frac{\partial V}{\partial x_k} - \frac{e}{c}\frac{\partial\bar{\Phi}_k}{\partial t}\right)\psi^*\psi + \frac{e}{c}\sum_l H_{kl}\, i_l \tag{78}$$

with

$$T_{kl} = \frac{\hbar^2}{4m}\left[-\psi^*\left(\frac{\partial}{\partial x_l} - \frac{i}{\hbar}\frac{e}{c}\bar{\Phi}_l\right)\left(\frac{\partial\psi}{\partial x_k} - \frac{ie}{\hbar c}\bar{\Phi}_k\psi\right) - \psi\left(\frac{\partial}{\partial x_l} + \frac{ie}{\hbar c}\bar{\Phi}_l\right)\left(\frac{\partial\psi^*}{\partial x_k} + \frac{ie}{\hbar c}\bar{\Phi}_k\psi^*\right)\right.$$
$$\left. + \left(\frac{\partial\psi}{\partial x_k} - \frac{ie}{\hbar c}\bar{\Phi}_k\psi\right)\left(\frac{\partial\psi^*}{\partial x_l} + \frac{ie}{\hbar c}\bar{\Phi}_l\psi^*\right) + \left(\frac{\partial\psi^*}{\partial x_k} + \frac{ie}{\hbar c}\bar{\Phi}_k\psi^*\right)\left(\frac{\partial\psi}{\partial x_l} - \frac{ie}{\hbar c}\bar{\Phi}_l\psi\right)\right] \tag{79}$$

or

$$T_{kl} = \frac{\hbar^2}{4m}\left\{\left[-\psi^*\frac{\partial^2\psi}{\partial x_l\partial x_k} - \psi\frac{\partial^2\psi^*}{\partial x_l\partial x_k} + \frac{\partial\psi}{\partial x_l}\cdot\frac{\partial\psi^*}{\partial x_k} + \frac{\partial\psi^*}{\partial x_l}\frac{\partial\psi}{\partial x_k}\right]\right.$$
$$\left. + \frac{2ie}{\hbar c}\left[\bar{\Phi}_k\left(\psi^*\frac{\partial\psi}{\partial x_l} - \psi\frac{\partial\psi^*}{\partial x_l}\right) + \bar{\Phi}_l\left(\psi^*\frac{\partial\psi}{\partial x_k} - \psi\frac{\partial\psi^*}{\partial x_k}\right)\right] + \frac{4e^2}{\hbar^2c^2}\bar{\Phi}_k\bar{\Phi}_l\,\psi^*\psi\right\} \tag{80}$$

so that the symmetry condition $T_{kl} = T_{lk}$ is again satisfied. In view of (74) we set

$$\overline{K}_k = \int \left[-\left(\frac{\partial V}{\partial x_k} + \frac{e}{c} \frac{\partial \bar{\Phi}_k}{\partial t} \right) \psi^* \psi + \frac{e}{c} \sum_l H_{kl} \dot{i}_l \right] dV \qquad (81)$$

$$\left[\frac{d\bar{x}_l}{dt} = \frac{\partial}{\partial t} \int x_l \psi^* \psi \, dV = \int \frac{dx_l}{dt} \psi^* \psi \, dV = \overline{\left(\frac{dx_l}{dt} \right)} = \int i_l \, dV \; ie \; i_l = \dot{x}_l \psi^* \psi \right]$$

and hence on account of $\int i_k \, dV = \frac{d\bar{x}_k}{dt}$ we have from (78)

$$m \frac{d^2 \bar{x}}{dt^2} = \overline{K}_k \qquad (82)$$

~~about~~ as the analogue of the equations of motion. Further with

$$\overline{x_k K_k} = \int \left[-x_k \left(\frac{\partial V}{\partial x_k} + \frac{e}{c} \frac{\partial \bar{\Phi}_k}{\partial t} \right) \psi^* \psi + \frac{e}{c} \sum_l H_{kl} x_k \dot{i}_l \right] dV \qquad (81')$$

we have in complete analogy with an earlier result that

$$m \frac{\partial}{\partial t} \int x_k \dot{i}_k \, dV = \int T_{kk} \, dV + \overline{x_k K_k}$$

From (79) it follows by partial integration that

$$\int T_{kk} \, dV = \frac{\hbar^2}{m} \int \left(\frac{\partial \psi^*}{\partial x_k} + \frac{ie}{\hbar c} \bar{\Phi}_k \psi^* \right) \left(\frac{\partial \psi}{\partial x_k} - \frac{ie}{\hbar c} \bar{\Phi}_k \psi \right) dV$$

$$= -\frac{1}{m} \overline{\left(p_k - \frac{e}{c} \bar{\Phi}_k \right)^2} = m \overline{\dot{x}_k^2}$$

The last two expressions can indeed be verified from the standpoint of a systematic operational calculus, which will be discussed later. With this reservation* we obtain

$$m \frac{\partial}{\partial t} \int x_k \dot{i}_k \, dV = m \overline{\dot{x}_k^2} + \overline{x_k K_k} \qquad (83)$$

Accordingly the analogue of the Virial theorem

In exactly the same way we obtain analogues of (70) and (71) viz

$$\frac{d}{dt}\overline{(\Delta x_k)^2} = 2\int (x_k - \bar{x}_k)\,\dot{i}_k\,dV \tag{84}$$

$$\frac{1}{2}\frac{d^2}{dt^2}\overline{(\Delta x_k)^2} = m\overline{(\dot{x}_k - \bar{\dot{x}}_k)^2} + \overline{(x_k - \bar{x}_k)K_k} \tag{85}$$

It is a well-known fact that the potentials Φ_k are arbitrary up to the addition of a gradient term, since through such an additional term the field strengths H_{kl} are not altered. It is accordingly an allowed substitution to put

$$\Phi_k' = \bar{\Phi}_k + \frac{\partial f}{\partial x_k} \tag{86}$$

wherein f is an arbitrary function of the space-coordinates. In case f contains the time explicitly one has then only to put simultaneously

$$V' = V - \frac{e}{c}\frac{\partial f}{\partial t} \tag{86'}$$

such that the expression (74) for the force should remain invariant. In fact we then have

$$\frac{\partial V'}{\partial x_k} + \frac{e}{c}\frac{\partial \Phi_k'}{\partial t} = \frac{\partial V}{\partial x_k} + \frac{e}{c}\frac{\partial \Phi_k}{\partial t}\;; \qquad H_{kl}' = H_{kl}$$

Since in the wave equation (76) the ~~fields~~ magnetic and electric field strengths do not enter but only the potentials V and Φ_k it might appear at first probable as to whether the physical results following from this wave equation might depend on the absolute values of the potentials. But it is not so; for if ψ be a solution of the wave equation (76) for the potential V and Φ_k one obtains a solution ψ' by [illegible] V' and Φ_k' from (86) or (86').

by the substitution

$$\psi' = \psi e^{\frac{ie}{\hbar c} f} \qquad (86^a)$$

The group of substitutions defined by (86), (86'), (86^a) is denoted as the guage-group, and magnitudes which remain unaltered by these substitutions as guage-invariant magnitudes. It is remarkable that not only the probability density $\psi^* \psi$ but also the current $\vec{i}$ given by (77) and the tensor T_{kl} as well defined by (79) are all guage-invariant quantities. From this point of view the wave equation (76), in particular the special choice of the Hamiltonian in this equation, must be considered as quite a natural one. On the otherhand it must be noticed that this equation depends essentially on the assumption that the field quantities V and $\vec{F}_k$ are account classical magnitudes of such a sort that any incidental influence of the quantum of action on the definition of these field quantities can be neglected.

(5) Interaction of several particles. Calculus of Operators: The method of treatment of a system consisting of a number of particles on the basis of quantum mechanics is of fundamental importance for the theory and is most characteristic for it. It shows on the one hand the fruitfulness of Schrödinger's idea in introducing a ψ-function satisfying a linear equation, and on the other hand the purely symbolic character of this function which is different in principle from the wave-functions of the classical theory (like surface waves of fluids, elastic waves and electro-magnetic waves)

In considering a system of many particles we do not obtain a sufficiently complete description of the system by prescribing the probability that one of the particles can be found at a specified position. Let us imagine for example a system consisting of two material particles which are enclosed in a closed box which is divided into two parts by a separating wall with a small opening which can be closed. By suddenly closing the opening and separating out the two halves one can determine in the case of each particle as to in what half of the box it is found at the particular moment. We do not however investigate how great is the probability of finding each particle in one or the other half of the box but how often it is that the particles are found in the same or different halves. Instead of the separating wall one might employ also a "microscope" observed with radiation of short waves, and instead of dividing a finite volume into only two parts one can achieve an arbitrarily fine division of the space. Let there be accordingly N particles present with coordinates $x_k^{(1)}, x_k^{(2)} \ldots x_k^{(N)}$ which we can also simply write as $q_1 \ldots q_f$ with $f = 3N$ denoting the number of degrees of freedom of the system; further we might simply denote the many-dimensional volume-element $dq_1 \ldots dq_f$ by dq. The fundamental assumptions for the description of a system with many particles can then be formulated in the following manner:

(1) At every instant time t, there exists a probability

$$W(q_1, \ldots q_f; t)\, dq \qquad (87)$$

that, simultaneously, the coordinates of the first particles lie in the region (q_k, q_k+dq_k) $(k=1,2,3)$, those of the second in (q_k, q_k+dq_k) $(k=4,5,6)$, ..., those of the Nth in (q_k, q_k+dq_k) $(k=f-2, f-1, f)$.

To explain this notion of probability it must be remarked that we have here assumed the possibility of distinguishing the particles from each other; the probability that the first particle is found in the position $x_k^{(1)}$, $x_k^{(1)}+dx_k^{(1)}$ and the second in $x_k^{(2)}$, $x_k^{(2)}+dx_k^{(2)}$ is in general different from the probability that the second is found in $x_k^{(1)}$, $x_k^{(1)}+dx_k^{(1)}$ and the first in $x_k^{(2)}+dx_k^{(2)}$, or what is the same thing, it depends entirely on the sequence order of $x_k^{(p)}$ in the arguments $q_1 \cdots q_f$ of W. Such a distinction is surely present when both the particles are of different kinds, for eg have different masses (like electron and proton, or like the nucleii of two different isotopes). The existence of exactly similar individuals in nature as for eg. two electrons or two protons or two α-particles compels us however to adopt a special treatment in this case which it has not yet been possible in present day quantum theory to bring to a direct expression. For similar particles one can only ask questions about the probability of finding one of the particles in $(x_k^{(1)}, x_k^{(1)}+dx_k^{(1)})$, one other in $(x_k^{(2)}, x_k^{(2)}+dx_k^{(2)})$, a last in $(x_k^{(N)}, x_k^{(N)}+dx_k^{(N)})$. If accordingly there are many similar particles, we can only consider such functions W significant as are symmetrical in the coordinates of the like particles. We come back to this case in § 14. Provisionally we shall ignore it.

except one, we are led to N new functions

$$W_1(x_1, x_2, x_3),\ W_2(x_4, x_5, x_6),\ \ldots\ W_N(x_{3N-2}, x_{3N-1}, x_{3N})$$

which give the probability of finding ~~one of the~~ a definite one of the particles at a definite position of space when the position of the remaining particles does not come into question. These functions say less about the system than the original function of f arguments in that the latter does not follow as a consequence of the former while the converse is true. (In the above example of the box with the two halves for eg it does not follow from the statement "It is equally probable for either particle to be in the first or second half of the box" that one can say anything about the relative abundance of the cases, "both particles are in the same half" and "both particles are in different halves".)

Only in one special case is the knowledge of the functions $W_1, \ldots W_N$ equivalent to knowing $W(q_1 q_2 \ldots q_f)$ viz when this function W resolves itself into a product

$$W(q_1 \ldots q_f) = W_1(q_1 q_2 q_3) W_2(q_4 q_5 q_6) \ldots W_N(q_{3N-2} q_{3N-1} q_{3N})$$

In this special case we say that the particles are statistically independent of each other.

The existence of the probability $W(q_1 \ldots q_f ; t)$ involves the assertion, or is possible only under the assumption, that the measurements of the positions of the particles do not mutually interfere in such a way that the applicability of the knowledge of the position of one of the particles to the prediction of other measurements (for eg the position of the particle at a later time) is not spoilt by the knowledge of the positions of the other particles. This question is intimately connected

with the question as to how far the simultaneity of the measurement of positions of different particles is essential for the existence of a probability. Or specifically, to find under what circumstances there exists a probability

$$W\left(x_k^{(1)}, t^{(1)}; x_k^{(2)}, t^{(2)}; \cdots; x_k^{(N)}, t^{(N)}\right) dq_1 \cdots dq_{3N} \qquad (88)$$

in order that the first particle might be found in the space element $x_k^{(1)}, x_k^{(1)} + dx_k^{(1)}$ at the time $t^{(1)}$, the second in $x_k^{(2)} + dx_k^{(2)}, x_k$ at time $t^{(2)}$, the Nth in $x_k^{(N)}, x_k^{(N)} + dx_k^{(N)}$ at time $t^{(N)}$. In general it when there appear interaction forces whatsoever between the particles, the mutual freedom from perturbations of the measurements is guaranteed if and only if the distance r_{ab} between any two particles (a, b) and the corresponding times satisfy

$$|t_a - t_b| < \frac{r_{ab}}{c}. \qquad (89)$$

The alteration of the force of interaction of particle $\underline{a}$ on the particle $\underline{b}$ which is excited by the measurement of position of $\underline{a}$ can propagate itself utmost with the velocity of light $\underline{c}$. In so far as one assumes in general the existence, in relativistic quantum mechanics, of a probability $W(x_1, x_2, x_3; t)\, dx_1 dx_2 dx_3$ for the position of a particle, there must be satisfied in general the relation (89) for the values of the arguments. In the non-relativistic wave mechanics it follows, since c is to be considered as infinite, that we can restrict ourselves to the case

$$t^{(1)} = t^{(2)} = \cdots = t^{(N)} = t$$

(2) As a natural generalisation of the analogous assumption for one particle we assume here also the existence of a function

$$\psi(q_1 \cdots q_n; t)$$

such that

$$W(q_1 \cdots q_f ; t)\, dq = \psi^* \psi\, dq . \tag{70}$$

This function ψ shall further satisfy an equation

$$-\frac{\hbar}{i}\frac{\partial \psi}{\partial t} = \underline{\underline{H}}\,\psi \tag{62}$$

where $\underline{\underline{H}}$ is a linear operator. The function $(\underline{\underline{H}}\psi)(q_1 \cdots q_f ; t)$ is thereby uniquely determined through the function $\psi(q_1 \cdots q_f ; t)$ for the same time t without it being necessary to have a knowledge of ψ at other times. To satisfy the condition

$$\frac{d}{dt}\int \psi \psi^* dq = 0$$

$\underline{\underline{H}}$ must be a Hermitian operator ie for two arbitrary functions ψ_1, ψ_2 which must satisfy certain regularity conditions

$$\int \psi_1^* \underline{\underline{H}}\, \psi_2\, dq = \int \psi_1 (\underline{\underline{H}}\, \psi_2)^*\, dq \tag{63'}$$

must hold.

(3) As generalisations of (24'') and (27) we assume also that

$$\varphi(p_1 \cdots p_f ; t) = \frac{1}{\sqrt{(2\pi\hbar)^f}} \int \psi(q_1 \cdots q_f ; t)\, e^{-\frac{i}{\hbar}(p_1 q_1 + \cdots + p_f q_f)}\, dq \tag{91}$$

with the inversion

$$\psi(q_1 \cdots q_f ; t) = \frac{1}{\sqrt{(2\pi\hbar)^f}} \int \varphi(p_1 \cdots p_f ; t)\, e^{+\frac{i}{\hbar}(p_1 q_1 + \cdots + p_f q_f)}\, dp ; \tag{91'}$$

accordingly

$$W(p_1 \cdots p_f ; t)\, dp = \varphi^* \varphi\, dp \tag{92}$$

is the probability that at time t the momentum of the particles lies between p_k and $p_k + dp_k$. Here we have put $dq = dq_1 \cdots dq_f$ and $dp = dp_1 \cdots dp_f$. Further,

the completeness relation

$$\int \varphi^* \varphi \, dp = \int \psi^* \psi \, dq \tag{93}$$

is also valid. In exact analogy with (47), (47') it follows from partial integration that when F is a rational integral function of the variables

$$\overline{F(p_1 \cdots p_f)}^* = \int \varphi^* F \varphi \, dp = \int \psi^* \left[F\left(\frac{\hbar}{i} \frac{\partial}{\partial q_1}, \cdots \frac{\hbar}{i} \frac{\partial}{\partial q_f} \right) \psi \right] dq \tag{94}$$

$$\overline{F(q_1 \cdots q_f)} = \int \psi^* F \psi \, dq = \int \varphi^* \left[F\left(i\hbar \frac{\partial}{\partial p_1}, \cdots, i\hbar \frac{\partial}{\partial p_f} \right) \varphi \right] dp \tag{94'}$$

We shall come back to the meaning of these relations at once.

As far as the choice of the Hamiltonian operator $\underline{\underline{H}}$ is concerned it is to be assumed first of all that in the case where no interaction between the particles arises, but arbitrary external forces might however act on the particles, the Hamiltonian must resolve itself into independent summands

$$\underline{\underline{H}} = \underline{\underline{H}}^{(1)} + \underline{\underline{H}}^{(2)} + \cdots + \underline{\underline{H}}^{(N)} \tag{95}$$

such that $H^{(1)}$ alters a function $\psi(x_k^{(1)})$ containing only the coordinates of the first particle, but transforms into itself a function containing the coordinates of the other particles. Then we have

$$\underline{\underline{H}}^{(1)} \left[\psi(q^{(1)}) \, \psi(q^{(2)} \cdots q^{(N)}) \right] = \left\{ \underline{\underline{H}}^{(1)} [\psi(q^{(1)})] \right\} \psi(q^{(2)} \cdots q^{(N)})$$

and correspondingly for the operators $H^{(2)} \cdots H^{(N)}$. Accordingly if

$$\psi^{(1)}(q^{(1)}), \cdots, \psi^{(N)}(q^{(N)})$$

be any solutions whatever of the wave equations

$$-\frac{\hbar}{i}\frac{\partial \psi^{(a)}}{\partial t} = \underline{\underline{H}}^{(a)}\psi^{(a)}, \quad (a = 1, 2 \cdots N)$$

of the isolated system, so is

$$\psi = \psi^{(1)}\psi^{(2)} \cdots \psi^{(N)} \tag{96}$$

a solution (but not the most general solution) of

$$-\frac{\hbar}{i}\frac{\partial \psi}{\partial t} = \underline{\underline{H}}\psi = \left[\underline{\underline{H}}^{(1)} + \underline{\underline{H}}^{(2)} + \cdots + \underline{\underline{H}}^{(N)}\right]\psi.$$

An additive resolution of the Hamilton operator into independent summands corresponds accordingly to a factorisation of the wave function into independent factors. This is connected with the fact that for statistically independent particles the probability is a product of factors. Since ψ is uniquely determined for all times by its course through a determined time t_0 we can accordingly say: when for an uncoupled system of particles the wave function resolves into factors at a given time this is also true for all times. It is also true therefore that if mechanically uncoupled particles are statistically independent at a given time t_0, they are so for all time.

On the basis of the previous article, we can write the Hamiltonian $\underline{\underline{H_0}}$ for uncoupled particles subjected to external forces. It is given by

$$\underline{\underline{H_0}} = \sum_{a=1}^{N}\left[-\frac{\hbar^2}{2m}\sum_{k=1}^{3}\left(\frac{\partial}{\partial x_k^{(a)}} - \frac{i}{\hbar}\frac{e^{(a)}}{c}\Phi^{(a)}(x_k^{(a)})\right)^2 + V^{(a)}(x_k^{(a)})\right] \tag{97}$$

When the force between the particles can be derived from a potential depending only on the positional co-ordinates and which can be written as $V(q_1 \cdots q_f)$ it is obvious that we should put

$$-\frac{\hbar}{i}\frac{\partial \psi}{\partial t} = \underline{\underline{H}}\psi = \underline{\underline{H_0}}\psi + V(q_1 \cdots q_f)\psi \qquad (98)$$

Under this assumption falls the Coulomb electric force, between charged particles, whose potential is given by

$$V = \sum_{(a,b)}{}' \frac{e_a e_b}{r_{ab}} \qquad (99)$$

[in this summation $a \neq b$ and each pair (a,b) is taken only once]. We shall consider the question of magnetic interaction of two particles when we discuss the relativistic quantum mechanics.

The expressions (97), (98), (99) provide in the case of non-relativistic wave mechanics, apart from a necessary extension concerning spin (§ 13), the foundation for the quantitative treatment of atomic- and molecular structure. Concerning its principal point, it is to be emphasised that in these expressions the potentials $\Phi^{(a)}$, $V^{(a)}$ and V are classical quantities; in particular the same is true of the Coulomb potential (99) which for its part is a consequence of Maxwell's equations. Accordingly, present day wave mechanics depends upon two fundamental assumptions. Firstly the equation (only symbolically understood) for material waves which can be logically considered as a generalisation of classical particle mechanics to the case of quantum mechanics. Secondly the Maxwell Electrodynamic equations which also require a quantum theoretic interpretation (B, §6). It would be further satisfactory if the notions of both these kinds were based on one single point of view, but this has not been found so far. This question is connected with the still unsolved problem

of the electrical elementary particles.

In this article we shall however consider the potentials simply as specified functions of space-time. It is quite easy to derive in our case the continuity equation (37) and the equation (45') for the time variation of the current. For this it is convenient to introduce instead of $e^{(a)}$, $m^{(a)}$, $\Phi^{(a)}(x_R^{(a)})$ where $R = 1, 2, 3$; $a = 1, \ldots N$, the symbols $e_k, m_k, \bar{\Phi}_k$ .. with $k = 1, 2 \ldots f$, so that for eg $m_1 = m_2 = m_3 = m^{(1)}$; $m_4 = m_5 = m_6 = m^{(2)}$. Then there is first in the f-dimensional configuration space a current vector i_k with f components ($k = 1, \ldots f$) whose physical significance is this, that for eg i_1 gives the probability that for a given phase positions of all the particles the first particle crosses a unit surface at right angles to x_1 either along the direction $-x_1$ to x_1 or in the reverse direction. This vector $\vec{i}$ is given in f-dimensional configuration space by

$$i_k = \frac{\hbar}{2 m_k i}\left(\psi^* \frac{\partial \psi}{\partial q_k} - \psi \frac{\partial \psi^*}{\partial q_k}\right) - \frac{1}{m_k}\frac{e_k}{c}\bar{\Phi}_k \psi^* \psi \qquad (100)$$

and satisfies the continuity equation

$$\frac{\partial (\psi^* \psi)}{\partial t} + \sum_{k=1}^{f} \frac{\partial i_k}{\partial q_k} = 0 \qquad (101)$$

Again for the stress-tensor in f-space we have analogous to (79) the expression

$$T_{\varkappa\lambda} = \frac{\hbar^2}{4 m_\lambda}\Big[-\psi^*\left(\frac{\partial}{\partial q_\lambda} - \frac{i e_\lambda}{\hbar c}\bar{\Phi}_\lambda\right)\left(\frac{\partial \psi}{\partial q_\varkappa} - \frac{i e_\varkappa}{\hbar c}\bar{\Phi}_\varkappa \psi\right)$$
$$- \psi\left(\frac{\partial}{\partial q_\lambda} + \frac{i e_\lambda}{\hbar c}\bar{\Phi}_\lambda\right)\left(\frac{\partial \psi^*}{\partial q_\varkappa} + \frac{i e_\varkappa}{\hbar c}\bar{\Phi}_\varkappa \psi^*\right)$$
$$+ \left(\frac{\partial \psi}{\partial q_\varkappa} + \frac{i e_\varkappa}{\hbar c}\bar{\Phi}_\varkappa \psi\right)\left(\frac{\partial \psi^*}{\partial q_\lambda} + \frac{i e_\lambda}{\hbar c}\bar{\Phi}_\lambda \psi^*\right)$$

$$+\left(\frac{\partial\psi^*}{\partial q_\varkappa}+\frac{ie_\varkappa}{\hbar c}\Phi_\varkappa\psi^*\right)\left(\frac{\partial\psi}{\partial q_\lambda}-\frac{ie_\lambda}{\hbar c}\Phi_\lambda\psi\right)\Bigg] \qquad (79')$$

The symmetry condition $T_{\varkappa\lambda}=T_{\lambda\varkappa}$ is here valid if $\varkappa$ and λ belong to the same particle. Analogous to (78) we have

$$m\frac{\partial i_\varkappa}{\partial t}=-\sum\frac{\partial T_{\varkappa\lambda}}{\partial q_\lambda}+\left(-\frac{\partial\left(V+\sum_a V^{(a)}\right)}{\partial q_\varkappa}-\frac{e_\varkappa}{c}\frac{\partial\Phi_\varkappa}{\partial t}\right)\psi^*\psi$$
$$+\frac{e_\varkappa}{c}\sum_\lambda\left(\frac{\partial\Phi_\lambda}{\partial q_\varkappa}-\frac{\partial\Phi_\varkappa}{\partial q_\lambda}\right)i_\lambda \qquad (78')$$

According to our assumption about Φ_R only three terms (those relating to the same particle) are different from zero in the last summation. Further one has

$$\frac{d\bar q_R}{dt}=\int i_R\,dV=\frac{1}{m_R}\left(\bar p_R-\frac{e_R}{c}\bar\Phi_R\right) \qquad (75')$$

$$m\frac{d^2\bar q_R}{dt^2}=\bar K_R \qquad (82')$$

where $\bar K_R$ is defined as in (81)

The last mentioned relations, the equations of motion, can be derived very generally from the wave equation with the help of the calculus of operators. We resume first of all with the relations (91), (91') which lead to the relations (94), (94') when F is a rational integral function. This lead these last leads us to ~~the momenta and co~~ correspond the make the momenta and coordinates correspond to operators which act as follows:

$$\underline{\underline{p_k}}\,\psi(q_1\cdots q_f)=\frac{\hbar}{i}\frac{\partial}{\partial q_k}\psi;\quad \underline{\underline{q_k}}\,\psi(q_1\cdots q_f)=q_k\psi \qquad (102)$$

$$p_R\,\varphi(p_1\cdots p_f)=p_k\varphi\;;\quad q_R\,\varphi(p_1\cdots p_f)=-\frac{\hbar}{i}\frac{\partial}{\partial p_k}\varphi \qquad (102')$$

From these follow the fundamental exchange relations (abbreviated hereafter as V-R)

$$\left.\begin{aligned} \underline{\underline{p}}_k \underline{\underline{q}}_l - \underline{\underline{q}}_l \underline{\underline{p}}_k &= \delta_{lk} \frac{\hbar}{i} \quad \left(\delta_{lk} = \begin{cases} 1 & \text{for } l = k \\ 0 & \text{for } l \neq k \end{cases}\right) \\ \underline{\underline{p}}_k \underline{\underline{p}}_l - \underline{\underline{p}}_l \underline{\underline{p}}_k &= 0 \\ \underline{\underline{q}}_k \underline{\underline{q}}_l - \underline{\underline{q}}_l \underline{\underline{q}}_k &= 0 \end{aligned}\right\} \qquad (103)$$

For example,

$$\underline{\underline{p}}_k \underline{\underline{q}}_k \psi = \frac{\hbar}{i} \frac{\partial}{\partial q_k} (q_k \psi); \quad \underline{\underline{q}}_k \underline{\underline{p}}_k \psi = q_k \frac{\hbar}{i} \frac{\partial}{\partial q_k} \psi$$

so that $$(\underline{\underline{p}}_k \underline{\underline{q}}_k - \underline{\underline{q}}_k \underline{\underline{p}}_k)\psi = \frac{\hbar}{i} \left(\frac{\partial}{\partial q_k} (q_k \psi) - q_k \frac{\partial \psi}{\partial q_k} \right) = \frac{\hbar}{i} \psi.$$

The same thing results when one employs $\varphi(p_1 \cdots p_f)$ for verification. In a similar way the remaining V-R in (103) can also be verified. This form of V-R is only another expression for the connection (91), (91') of $\varphi(p)$ with $\psi(q)$.

It is further to be emphasized that the $\underline{\underline{p}}_k$ and $\underline{\underline{q}}_k$ are Hermitian (linear) operators. Such operators are defined as those satisfying the relation

$$\int \psi_1^* (\underline{\underline{H}} \psi_2) \, dV = \int \psi_2 (\underline{\underline{H}} \psi_1)^* \, dV \qquad (63)$$

for arbitrary functions ψ_1 and ψ_2, and it can be readily confirmed that the operators (102) satisfy the relation (63).

[The confirmation is immediate if by partial integration we consider the equivalent relation with $\psi_1 = \psi_2 = \psi$]

We mention further that by applying (63) twice we have for two operators

assumed Hermitean

$$\int (\underline{\underline{H_1}}\,\psi_1)^* (\underline{\underline{H_2}}\,\psi_2)\, dV = \int \psi_2\, (\underline{\underline{H_2}}\,\underline{\underline{H_1}}\,\psi_1)^*\, dV$$

$$\int (\underline{\underline{H_2}}\,\psi_2)^* (\underline{\underline{H_1}}\,\psi_1)\, dV = \int \psi_1\, (\underline{\underline{H_1}}\,\underline{\underline{H_2}}\,\psi_2)^*\, dV$$

[~~The left hand side of either of the above is the conjugate~~

[The integrand in the left hand side of either of the above equations is the complex conjugate of the other, and hence]

$$\int \psi_2\, (\underline{\underline{H_2}}\,\underline{\underline{H_1}}\,\psi_1)^* dV = \int \psi_1^*\, (\underline{\underline{H_1}}\,\underline{\underline{H_2}}\,\psi_2)\, dV \qquad (104)$$

From this it follows: If $\underline{\underline{H_1}}$ and $\underline{\underline{H_2}}$ be two Hermitian linear operators the same is true of

$$\underline{\underline{F}} = \underline{\underline{H_1}}\,\underline{\underline{H_2}} + \underline{\underline{H_2}}\,\underline{\underline{H_1}} \qquad (105)$$

and $$\underline{\underline{G}} = i\,(\underline{\underline{H_1}}\,\underline{\underline{H_2}} - \underline{\underline{H_2}}\,\underline{\underline{H_1}}) \qquad (105')$$

$$\left[\int \psi_1^* (\underline{\underline{F}}\,\psi_2)\, dV = \int \psi_1^* (\underline{\underline{H_1}}\,\underline{\underline{H_2}}\,\psi_2)\, dV + \int \psi_1^* (\underline{\underline{H_2}}\,\underline{\underline{H_1}}\,\psi_2)\, dV \right.$$

$$= \int \psi_2\, (\underline{\underline{H_2}}\,\underline{\underline{H_1}}\,\psi_1)^* dV + \int \psi_2\, (\underline{\underline{H_1}}\,\underline{\underline{H_2}}\,\psi_1)^* dV \qquad \text{(using (104))}$$

$$\left. = \int \psi_2\, (\underline{\underline{F}}\,\psi_1)^* dV. \quad \text{An identical proof holds for } \underline{\underline{G}} \right]$$

If in particular $\underline{\underline{H_1}}$ and $\underline{\underline{H_2}}$ commute, then $\underline{\underline{H_1}}\,\underline{\underline{H_2}}$ is also hermitian (from (105')), so that any rational integral function of $\underline{\underline{H_1}}$ is also hermitian. If $\underline{\underline{A}}$ and $\underline{\underline{B}}$ be two linear operators, we often write as an abbreviation

$$[\underline{\underline{A}}, \underline{\underline{B}}] \equiv i(\underline{\underline{A}}\,\underline{\underline{B}} - \underline{\underline{B}}\,\underline{\underline{A}}). \tag{106}$$

Then we have

$$[\underline{\underline{A_1}}\,\underline{\underline{A_2}}, \underline{\underline{A_3}}] \equiv \underline{\underline{A_1}}[\underline{\underline{A_2}}, \underline{\underline{A_3}}] + [\underline{\underline{A_1}}, \underline{\underline{A_3}}]\,\underline{\underline{A_2}} \tag{107}$$

$$[[\underline{\underline{A_1}}, \underline{\underline{A_2}}], \underline{\underline{A_3}}] + [[\underline{\underline{A_2}}, \underline{\underline{A_3}}], \underline{\underline{A_1}}] + [[\underline{\underline{A_3}}, \underline{\underline{A_1}}], \underline{\underline{A_2}}] \equiv 0 \tag{108}$$

Let, now, $\underline{\underline{F}}$ be an arbitrary Hermitian linear operator which does not contain the time explicitly, and $\underline{\underline{H}}$ the Hamiltonian operator. We shall calculate the time-variation of the mean value ("Expectation-value") of

$$\bar{F} = \int \psi^* (\underline{\underline{F}}\,\psi)\, dV \tag{109}$$

We have the result

$$\hbar \frac{d\bar{F}}{dt} = \hbar \int \frac{\partial \psi^*}{\partial t} (\underline{\underline{F}}\,\psi)\, dV + \hbar \int \psi^* \left(\underline{\underline{F}} \frac{\partial \psi}{\partial t}\right) dV$$

$$= i \int (\underline{\underline{H}}\,\psi)^* (\underline{\underline{F}}\,\psi)\, dV - i \int \psi^* (\underline{\underline{F}}[\underline{\underline{H}}\,\psi])\, dV$$

$$= i \int \psi^* [(\underline{\underline{H}}\,\underline{\underline{F}})\,\psi]\, dV - i \int \psi^* [(\underline{\underline{F}}\,\underline{\underline{H}})\,\psi]\, dV. \quad \text{(since F is Hermitian)}$$

Accordingly

$$\hbar \frac{d\bar{F}}{dt} = \int \psi^* ([\underline{\underline{H}}, \underline{\underline{F}}]\,\psi)\, dV = \overline{[\underline{\underline{H}}, \underline{\underline{F}}]} = i\,\overline{(\underline{\underline{H}}\,\underline{\underline{F}} - \underline{\underline{F}}\,\underline{\underline{H}})} \tag{110}$$

Now for every function $F(p_1 \cdots p_f)$ of p alone, we have

$$\underline{\underline{F}}\,\underline{\underline{p}}_k - \underline{\underline{p}}_k\,\underline{\underline{F}} = 0\,; \quad \underline{\underline{F}}\,\underline{\underline{q}}_k - \underline{\underline{q}}_k\,\underline{\underline{F}} = \frac{\hbar}{i} \frac{\partial \underline{\underline{F}}}{\partial \underline{\underline{p}}_k} \tag{111}$$

of which the first is immediately obvious. The second formula is true for

$F = p_i$ and for $F = p_K$; further if it be true for F_1 and F_2 it is true for $F_1 + F_2$ and also for $F_1 \cdot F_2$ as can be deduced from (107). Consequently we have proved the assertion (111) for every rational integral function F of p. Similarly in view of the definition $p_K = \frac{\hbar}{i} \frac{\partial}{\partial q_K}$, we have for every function $G(q_1 \cdots q_f)$ of q alone

$$\underline{\underline{p_k}}\,\underline{\underline{G}} - \underline{\underline{G}}\,\underline{\underline{p_K}} = \frac{\hbar}{i} \frac{\partial \underline{\underline{G}}}{\partial \underline{\underline{q_K}}} \; ; \quad \underline{\underline{q_K}}\,\underline{\underline{G}} - \underline{\underline{G}}\,\underline{\underline{q_K}} = 0 \tag{112}$$

From (111) and (112) together it follows that for every function

$$\underline{\underline{H}}(p, q) = \underline{\underline{F}}(p_1 \cdots p_f) + \underline{\underline{G}}(q_1, \cdots q_f) \tag{113}$$

where F is rational integral and G arbitrary

$$\underline{\underline{H}}\,\psi(q) = \left[\underline{\underline{F}}\left(\frac{\hbar}{i}\frac{\partial}{\partial q_1}, \cdots \frac{\hbar}{i}\frac{\partial}{\partial q_f}\right) + \underline{\underline{G}}(q_1 \cdots q_f)\right]\psi$$

$$\underline{\underline{H}}\,\underline{\underline{p_K}} - \underline{\underline{p_K}}\,\underline{\underline{H}} = -\frac{\hbar}{i}\frac{\partial \underline{\underline{H}}}{\partial \underline{\underline{q_K}}} \; ; \quad \underline{\underline{H}}\,\underline{\underline{q_K}} - \underline{\underline{q_K}}\,\underline{\underline{H}} = \frac{\hbar}{i} \cdot \frac{\partial \underline{\underline{H}}}{\partial \underline{\underline{p_K}}} \tag{114}$$

Finally on the basis of the definition of $\underline{\underline{p_K}}$ and $\underline{\underline{q_K}}$ it is also easy to prove the above formulae for a function of the form

$$\underline{\underline{H}} = \underline{\underline{F}}(p_1 \cdots p_f) + \sum_K \left[\underline{\underline{A_K}}(q)\,\underline{\underline{p_K}} + \underline{\underline{p_K}}\,\underline{\underline{A_K}}(q)\right] + \underline{\underline{G}}(q_1 \cdots q_f) \tag{113'}$$

(Notice the symmetrising of the sequence of the factors A_K, p_K. This is necessary since $\underline{\underline{H}}$ is to be Hermitian. See (105))

In this form the Hamiltonian function is expressed in Cartesian coordinates which is what we have been using so far.

Putting $F = p_K$ and $F = q_K$ successively in (110) we deduce from (114)

$$\frac{d\bar{p}_k}{dt} = -\overline{\left(\frac{\partial H}{\partial q_k}\right)}\,; \quad \frac{d\bar{q}_k}{dt} = +\overline{\left(\frac{\partial H}{\partial p_k}\right)} \tag{115}$$

for the mean values of the concerned magnitudes over the wave packet of an arbitrary solution of the wave equation. Again putting $\underline{\underline{F}} = \underline{\underline{H}}$ in (110) we have because of $[H, H] \equiv 0$; the relation

$$\frac{d\bar{H}}{dt} = 0 \; ; \quad \bar{H} = \text{constant} \tag{116}$$

for the case that H does not contain the time explicitly. Here we perceive the expression of the energy theorem since $\bar{H}$ can be interpreted as the mean value of the energy over the wave packet. Likewise follows for the total momentum

$$\bar{P} = \overline{\sum_k p_k} \quad \text{and} \quad \frac{d\bar{P}}{dt} = -\overline{\left(\sum_k \frac{\partial}{\partial q_k}\right) H}$$

which expression vanishes when $\underline{\underline{H}}$ depends explicitly only on the differences of the coordinates $q_k - q_i$. Further for the angular momentum, firstly in the case of absence of a magnetic field,

$$\underline{\underline{J}}_{ik} = \sum_{a=1}^{N} \left(\underline{\underline{q}}_i^{(a)} \underline{\underline{p}}_k^{(a)} - \underline{\underline{q}}_k^{(a)} \underline{\underline{p}}_i^{(a)} \right) \qquad \left(J_{ik} = -J_{ki} \; ; \; i, k = 1, 2, 3 \right) \tag{117}$$

[(a) = particle-index which runs from 1 to N]

$$\frac{d\bar{J}_{ik}}{dt} = -\overline{\sum_{a=1}^{N} \left[q_i^{(a)} \frac{\partial V}{\partial q_k^{(a)}} - q_k^{(a)} \frac{\partial V}{\partial q_i^{(a)}} \right]} \tag{118}$$

[using (110) and (114), and use $\underline{\underline{H}} = \underline{\underline{F}}(p) + \underline{\underline{V}}(q)$

where, as in the case of classical mechanics, the right hand side vanishes when the potential energy of the system is invariant for a riged rotation

of the whole system in space. In the case where an external magnetic field is present

$$\frac{d\bar{q}_x}{dt} = \frac{1}{m}\left(\bar{p}_x - \frac{e}{c}\bar{\Phi}_x\right) = \int i_x\, dq \qquad (119)$$

where i_x is defined by (100). According to our definition of mean value it further follows with $H_{x\lambda} = \frac{\partial \Phi_\lambda}{\partial q_x} - \frac{\partial \Phi_x}{\partial q_\lambda}$ that

$$\int H_{x\lambda}\, i_\lambda\, dq = \frac{1}{2}\overline{\left(H_{x\lambda}\dot{q}_\lambda + \dot{q}_\lambda H_{x\lambda}\right)} = \frac{1}{2m}\overline{\left(H_{x\lambda}\, p_\lambda + p_\lambda H_{x\lambda}\right)} - \frac{e}{mc} H_{x\lambda}\bar{\Phi}_\lambda$$

accordingly,

$$m\frac{d^2\bar{q}_x}{dt^2} = -\frac{\partial}{\partial q_k}\overline{\left(V + \sum_a V^{(a)}\right)} - \frac{e_x}{c}\left(\frac{\partial \bar{\Phi}_x}{\partial t}\right) + \frac{e_x}{c}\cdot\frac{1}{2}\sum_\lambda \overline{\left(H_{x\lambda}\dot{q}_\lambda + \dot{q}_\lambda H_{x\lambda}\right)} = \bar{K}_x$$

and with

$$\left.\begin{aligned} \underline{\underline{J}}_{ik} &= \sum_{a=1}^{N} m^{(a)}\left(q_i^{(a)}\cdot q_k^{(a)} - q_k^{(a)}\cdot q_i^{(a)}\right) \\ &= \sum_{a=1}^{N}\left[\left(q_i^{(a)} p_k^{(a)} - p_k^{(a)} q_i^{(a)}\right) - \frac{e^{(a)}}{c}\left(q_i^{(a)}\bar{\Phi}_k^{(a)} - q_k^{(a)}\bar{\Phi}_i^{(a)}\right)\right] \end{aligned}\right\} \qquad (117')$$

$$\overline{J_{ik}} = \sum_{a=1}^{N} m^{(a)}\int\left[q_i^{(a)}\cdot i_k^{(a)} - q_k^{(a)}\cdot i_i^{(a)}\right] dq \qquad (117'')$$

$$\frac{d\overline{J}_{ik}}{dt} = \frac{1}{2}\sum_{(a)}\left[\overline{\left(q_i^{(a)} K_k^{(a)} - q_k^{(a)} K_i^{(a)}\right)} + \overline{\left(K_k^{(a)} q_i^{(a)} - K_i^{(a)} q_k^{(a)}\right)}\right] \qquad (120)$$

where by $\underline{\underline{K_k^{(a)}}}$ is understood the operator of the concerned force-component. The last result also follows directly from (78'). The right-hand side of (120) vanishes again when the system possesses rotational symmetry about an axis perpendicular to the $(x_i x_k)$-plane. (Cf. §13).

We have still got to consider the case where we use coordinates

other than Cartesians. Since the classical Hamiltonian function in its general form is a quadratic in p and any function of q, there enters in general an ambiguity in the order of the factors $f(q)$ and p_k. This order cannot be determined other than by conversion to cartesian coordinates. on the otherhand it is possible to give a reasonable rule for the formation of the partial differential coefficients with respect to p_k and q_k of such general expressions. We must thus definitely assume that in general for a product of two functions $F_1 \cdot F_2$ we shall always have

$$\frac{\partial}{\partial x}(\underline{\underline{F_1}}\,\underline{\underline{F_2}}) = \frac{\partial \underline{\underline{F_1}}}{\partial x}\underline{\underline{F_2}} + \underline{\underline{F_1}}\frac{\partial \underline{\underline{F_2}}}{\partial x} \qquad (121)$$

including the order of the factors; wherefrom by induction to a product of arbitrarily many factors it follows that

$$\frac{\partial}{\partial x}(\underline{\underline{F_1}} \cdots \underline{\underline{F_N}}) = \frac{\partial \underline{\underline{F_1}}}{\partial x}\underline{\underline{F_2}} \cdots \underline{\underline{F_N}} + \underline{\underline{F_1}}\frac{\partial \underline{\underline{F_2}}}{\partial x}\underline{\underline{F_3}} \cdots \underline{\underline{F_N}} + \cdots + \underline{\underline{F_1}}\,\underline{\underline{F_2}} \cdots \underline{\underline{F_{N-1}}}\frac{\partial \underline{\underline{F_N}}}{\partial x} \qquad (121')$$

in which we can substitute for x any one of the variables $p_1 \cdots q_f$. In this case (114) is in general correct when $\underline{\underline{H}}$ is rational integral in p and arbitrary in q, and on account of (110), (115) is again a consequence of the wave equation.

We can now formulate the wave equation in arbitrary curvilinear coordinates. Let the line-element be

$$dS^2 = g_{\chi\lambda}\, dq_\chi\, dq_\lambda$$

(summation convention being adopted) where $g_{\chi\lambda} = g_{\lambda\chi}$ is an arbitrary function of q_χ, and the mass-factor is considered as included in $g_{\chi\lambda}$. Let $g^{\chi\lambda}$ be the

matrix reciprocal to $g_{\chi\lambda}$ and $D = \sqrt{|g|}$ the square root of the determinant $|g| = |g_{\chi\lambda}|$ of the $g_{\chi\lambda}$. Then in these coordinates the wave equation runs as

$$-\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = \frac{1}{2}\cdot\frac{1}{D}\left(\frac{\hbar}{i}\frac{\partial}{\partial q_\chi} + A_\chi\right) D g^{\chi\lambda}\left(\frac{\hbar}{i}\frac{\partial}{\partial q_\lambda} + A_\lambda\right)\psi + V\psi \qquad (97^*)$$

where A_χ is the vector potential multiplied by $-\frac{e_\chi}{c}$.

[ingeneral relativity $\square = \frac{1}{\sqrt{g}}\frac{\partial}{\partial x_k}\left(\sqrt{g}\, g^{ik}\frac{\partial}{\partial x_i}\right)$ · See Pauli - Ency. article p. 607 eq^n (144)]

with

$$\rho = D\psi^*\psi$$

$$i^\chi = D g^{\chi\lambda}\left[\psi^*\left(\frac{\hbar}{i}\frac{\partial\psi}{\partial q_\lambda} + A_\lambda\psi\right) - \psi\left(-\frac{\hbar}{i}\frac{\partial\psi^*}{\partial q_\lambda} + A_\lambda\psi^*\right)\right]$$

the continuity equation becomes

$$\frac{\partial\rho}{\partial t} + \frac{\partial i^\chi}{\partial q_\chi} = 0.$$

On account of the appearance of the factor D in the density function, an operator $\underline{\underline{F}}$ is said to be hermitian if

$$\int D\psi^*\left(\underline{\underline{F}}\psi\right)dq = \int D(F\psi)^*\psi\, dq.$$

The momentum operator will be hermitian in this sense and besides satisfies the V-R

$$\underline{\underline{p}}_\chi\underline{\underline{q}}_\chi - \underline{\underline{q}}_\chi\underline{\underline{p}}_\chi = \hbar/i \text{ , and}$$

accordingly must satisfy

$$\underline{\underline{p}}_\chi\psi = \frac{\hbar}{i}\frac{1}{\sqrt{D}}\frac{\partial\sqrt{D}\,\psi}{\partial q_\chi}$$

The relations of this operator to the wave equation and to the current can be

readily set up.

In the special case of spatial polar coordinates

$$ds^2 = m\left(dr^2 + r^2 d\vartheta^2 + r^2 \sin^2\vartheta\, d\varphi^2\right);$$

accordingly

$$D = r^2 \sin\vartheta\,;\quad g^{rr} = \frac{1}{m}\,;\quad g^{\vartheta\vartheta} = \frac{1}{m}\cdot\frac{1}{r^2}\,;\quad g^{\varphi\varphi} = \frac{1}{m}\cdot\frac{1}{r^2\sin^2\vartheta}$$

For lateral applications it is to be noticed that in this case

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{df}{dr}\right) = \frac{1}{r}\frac{d^2}{dr^2}(rf)$$

Putting

$$\underline{\underline{p}}_r\,\psi = \frac{\hbar}{i}\,\frac{1}{r}\,\frac{d}{dr}(r\psi)\,;\quad \underline{\underline{P}}^2 = -\hbar^2\left(\frac{1}{\sin\vartheta}\,\frac{\partial}{\partial\vartheta}\sin\vartheta\,\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\,\frac{\partial^2}{\partial\varphi^2}\right) \qquad (97'^*)$$

we can write the Hamiltonian operator, according to (97*) in the simple form

$$\underline{\underline{H}} = \frac{1}{2m}\left(\underline{\underline{p}}_r^{\,2} + \frac{\underline{\underline{P}}^2}{r^2}\right) + V \qquad (97''^*)$$

This method of writing was often employed in the older books on quantum-mechanics.

(6) Stationary states as an Eigenwert problem: Among the solutions of the general wave equation

$$-\frac{\hbar}{i}\,\frac{\partial\psi}{\partial t} = \underline{\underline{H}}\left(\frac{\hbar}{i}\,\frac{\partial}{\partial q}\,,\,q\right)\psi \qquad (62)$$

those for which the density $\psi^*\psi$ as well as the current density are time constants have a special interest. We shall also assume in passing that the field quantities V, F_k appearing in $\underline{\underline{H}}$ do not contain the time explicitly. The concerned solutions then correspond to the so called stationary states of the system. Since $\psi^*\psi$ as well as $\psi^*\frac{\partial\psi}{\partial x_k} - \psi\frac{\partial\psi^*}{\partial x_k}$ must both be independent

$$\psi = u(q)\, e^{-if(t)}$$

where u is independent of t, and f of q. From (62) it follows that

$$\hbar \frac{df}{dt} u(q) = \underline{\underline{H}}\left[u(q)\right]$$

and this is obviously only possible when $\frac{df}{dt}$ is independent of the time. We can accordingly write

$$\psi_E = u(q)\, e^{-\frac{i}{\hbar} Et} \qquad (122)$$

$$\underline{\underline{H}}\left(\frac{\hbar}{i}\frac{\partial}{\partial q}, q\right) u = Eu \qquad (123)$$

We are here dealing with a homogeneous linear differential equation which contains a parameter. As is well known such differential equations do not always possess regular solutions for all values of E, and we therefore speak of an Eigenwert-problem. To fix up the regularity conditions of the problem let us start with the equation

$$\int v^* (\underline{\underline{H}} u)\, dq = \int u (\underline{\underline{H}} v)^*\, dq \qquad (124)$$

which is valid for two arbitrary functions u and v. Of the solutions of (123) the ~~solutions~~ functions allowed must satisfy the requirement that this "Hermiticity" or "complex-self-adjointness" of $\underline{\underline{H}}$ is not disturbed through singular points. In particular (124) will be valid when one of the functions is regular. Regarding the region of values of q and the region of function u, we might make otherwise still very general assumptions. [In general by dq is understood the volume differential $\rho(q)\, dq_1 \ldots dq_f$ with a chosen density function $\rho(q)$] For eg we can treat of angular momenta magnitudes varying from 0 to 2π or 0 to 4π

for rotations of rigid bodies. Or we can treat of functions in a restricted interval, say $(-1, +1)$ which assume the same values for -1 and $+1$, or again functions defined in the half-space $(0, \infty)$ which must vanish for $q_i = 0$. (124) must always be satisfied for the regions of the functions restricted by the boundary and regularity conditions. Thereby it is necessary that u and v should be everywhere regular. On account of the significance of $\psi^* \psi = u u^*$ as the probability density it is obvious that one should require

$$\int u u^* dq \qquad (125)$$

to exist (be finite) when integrated over the whole domain of q. In many cases discrete Eigenvalues E are distinguished by this condition. In the case of continuous E-values the condition (125) is not so strong as can be gathered from the case of force-free particles. A solution of

$$-\frac{\hbar^2}{2m} \Delta u = E u$$

is the plane wave $u_{p_1 \cdots p_f} = e^{\frac{i}{\hbar}(p_1 q_1 + \cdots + p_f q_f)}$, wherein $p_1 \cdots p_f$ appear as integration constants. Plainly for these waves the condition (125) is not fulfilled. In fact plane waves represent physically a limiting singular case because here, the probability of finding a particle outside a definite finite volume is infinitely much larger than the probability of finding it inside; only the coefficient of the ratio of the probabilities of finding the particle in two different finite regions has a determinate value. As already shown in §2 these singularities however vanish when one considers a wave packet. If

the integral

$$\bar{u}_{p_k', p_k''} = \int_{p_k'}^{p_k''} dp_1 \cdots dp_f \; u_{p_1 \cdots p_f}$$

then the integral of $\bar{u}\,\bar{u}^*$ exists over the whole of q-space exists.

[This denotes an elementary wave packet of the form (24) but not taken over the whole of momentum space, but for the range $\Delta p_k' \to 0$]

In the case where the eigen-values functions depend continuously on certain parameters $\lambda_1, \lambda_2, \ldots$ (denoted shortly by λ without indices), we shall substitute (125) by the condition that for

$$\bar{u}_{\lambda', \lambda''} = \int_{\lambda'}^{\lambda''} u_\lambda(q)\, d\lambda \qquad (126)$$

(where $d\lambda$ is the abbreviation for $d\lambda_1 \cdots d\lambda_n$) the integral

$$\int \bar{u}^*_{\lambda', \lambda''}(q)\, \bar{u}_{\lambda', \lambda''}(q)\, dq \qquad (127)$$

exists. We shall then take the relation (124) to hold $\int$ over the whole of q-space for these "elementary packets" $\bar{u}_{\lambda', \lambda''}$.

We can arrive at a unitary treatment of discrete and continuous eigenvalues if we put

$$\bar{u}_\lambda = \int_{\lambda_0}^{\lambda} u_\lambda(q)\, d\lambda + \sum_{p=\lambda_1}^{\lambda_n} u_p(q) \qquad (126')$$

where the integral is extended over the continuous eigen-values lying in the interval $(\lambda_0 \leqq \lambda' < \lambda)$, and the sum over the discrete eigen-values lying in the same interval. One can vary $\bar{u}_\lambda$ discontinuously by 1. Still there exists for every

~~for every~~ continuous function $f(\lambda)$ the Stieltjes integral

$$\int_{\lambda_0}^{\lambda} f(\lambda)\, d\bar{u}_\lambda = \int_{\lambda_0}^{\lambda_\beta} f(\lambda)\, u_\lambda(q)\, d\lambda + \sum_{p=\lambda_1}^{\lambda_n} u_p\, f(\lambda_p)$$

We can now characterise (completely independently of the existence of u_λ) the functions $\bar{u}_\lambda$ obtained by altering u_λ discontinuously by the generalisation of (123) to the corresponding equation

$$\left(\underline{\underline{H}}\,\bar{u}_{\lambda''}\right) - \left(\underline{\underline{H}}\,\bar{u}_{\lambda'}\right) = \int_{\lambda'}^{\lambda''} \left[\underline{\underline{H}}\, d\bar{u}_\lambda\right] = \int_{\lambda'}^{\lambda''} E(\lambda)\, d\bar{u}_\lambda \qquad (123')$$

where the values of E appear as discrete eigen-values at the discontinuities $\lambda_1, \lambda_2 \cdots$ of $\bar{u}_\lambda$.

To investigate the singularities (of u and v) consistent with (124) it is useful to start with the equation

$$\int \left[v^* \underline{\underline{H}}\, u - u\left(\underline{\underline{H}}\, v\right)^*\right] dq = \oint i_N(v^*, u)\, df \qquad (128)$$

which follows from the integration of the continuity equation

$$v^* \underline{\underline{H}}\, u - u\left(\underline{\underline{H}}\, v\right)^* = \mathrm{Div}\, \vec{i}\,(v^*, u),$$

over a finite volume of the ~~coordinate space~~ q-space. Here, $\vec{i}\,(\psi^*, \psi)$ is the usual current density from which is obtained $\vec{i}\,(v^*, u)$ by the formal substitutions $\psi^* \to v^*$, $\psi \to u$. The Div is to be understood in f-dimensional space (possibly in curvilinear coordinates), while the surface integral on the right-hand side of (128), in which i_N denotes the component normal component of $\vec{i}$, is extended over the closed surface enclosing the volume. In special cases the left-hand side of (128) is a one-dimensional integral, the right-hand

side degenerates into the difference of the values of i at the integration limits $q_1, q_2, \ldots$ At the points where the potential function entering $\underline{H}$ is singular it is required that the contributions to the surface integral arising from the enclosing of the singularities by small regions can be made as small as possible.

We can then ~~consider~~ make deduce easily the assertions for the following cases: –

(a) Let a one-dimensional problem with the Hamilton function

$$\frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx} - \frac{e}{c}\bar{\Phi}(x)\right)^2 + V(x)$$

be given. Let $\bar{\Phi}(x)$ or $V(x)$ or both functions be discontinuous at a point x_0. Since here it is necessary that

$$i(v^*, u) = \frac{1}{2m}\left[v^*\left(\frac{\hbar}{i}\frac{du}{dx} - \frac{e}{c}\bar{\Phi}(x)u\right) - u\left(\frac{\hbar}{i}\frac{dv^*}{dx} + \frac{e}{c}\bar{\Phi}(x)v^*\right)\right]$$

it is desirable that

$$\frac{du}{dx} - \frac{ihe}{c}\bar{\Phi}(x)u \text{ be continuous, } u \text{ continuous for } x = x_0 \qquad (129)$$

This must be true for all the functions considered here, and hence also for $V(x)$.

(b) Let V be singular for a particle in ordinary space. The integral $\oint i_N df$ for a small sphere about the origin is

$$r^2 \int\left[v^*\left(\frac{\hbar}{i}\frac{\partial u}{\partial r} - \frac{e}{c}\bar{\Phi}_r u\right) - u\left(\frac{\hbar}{i}\frac{\partial v^*}{\partial r} + \frac{e}{c}\bar{\Phi}_r v^*\right)\right] d\Omega$$

Let all the v and u be of the form $\bar{v}/r^\alpha$, $\bar{u}/r^\alpha$ wherein $\bar{v}$ and $\bar{u}$ are regular at the origin (perhaps they might vanish, but it is not usually necessary to consider this), so that we see that* $2-2\alpha > 0$, accordingly $\alpha < 1$

ie u and v must tend to ∞ for $r = 0$ more slowly than $1/r$; an eigenfunction for the limit $(ru) = A \neq 0$ is not allowed (although for such a function $\int_0^\infty u^* u r^2 dr$ exists). [ie $\alpha = 1$ also is not allowed, although $\int_0^\infty \bar{u}^* u \cdot dr$ may exist]

We obtain accordingly a well-defined eigenwertproblem and hence a natural and non-arbitrary method for determining the possible discrete or continuous eigen-values of the system. This method is due to Schrödinger who has shown at the same time that for an electron with the charge $-e$ under the influence of a fixed nucleus of charge $+Ze$, and accordingly with the potential energy $V = -\frac{Ze^2}{r}$ one can deduce from the corresponding wave equation

$$+\frac{\hbar^2}{2m} \Delta u + \left(E + \frac{Ze^2}{r}\right) u = 0$$

the negative discrete Energy-eigen values $-Rh/1^2$, $-Rh/2^2$, . . $-Rh/n^2$, . . . and there the continuous positive eigen values $(0 \leqq E < +\infty)$. Here

$$R = \frac{me^4}{4\pi\hbar^3} Z^2$$

which is the Rydberg constant multiplied by the square of the nuclear charge-number (atomic number). (Since here a discrete and a continuous eigenwert-problem appear mixed up, the behaviour of the potential function for large distances, its slow increase towards zero for negative values are essential. on the other hand the singularity of V at the origin is not important since the point-nucleus can equally well be substituted by a small charged sphere).

The simplest example of a system with only discrete eigen-values is the harmonic oscillator which, in the one dimensional case, has the potential energy

$$V = \frac{1}{2} m \omega^2 x^2,$$

and in the three dimensional ~~case~~ isotropic case

$$V = \frac{1}{2} m \omega^2 r^2$$

with ω = circle-frequency of the oscillator. The energy-values are

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega \qquad n = 1, 2, 3, \ldots$$

for the linear,

$$E_n = \left(n + \tfrac{3}{2}\right) \hbar \omega \qquad n = 1, 2, 3,$$

for the isotropic spatial oscillator. In the case considered here (as also in the force free case) the series of eigen values is limited below, and there is accordingly a least eigen-value. That this is not always the case is shown by the example

$$V = - Fx$$

which corresponds to a constant force in the $+x$ direction.

As an example of calculations in curvilinear coordinates we shall consider here the special case of polar coordinates for the problem of the Hydrogen atom since the problem of a particle in a central field ie in a field for which the potential energy $V(r)$ depends only on the distance of the particle from a fixed centre is of special importance. [Cfr. eqns (97'*) & (97''*) of p. 421]. The operator Δ assumes in polar coordinates the form

$$\Delta u \equiv \frac{1}{r^2} \frac{d^2}{dr^2}(ru) + \frac{1}{r^2} \underline{\underline{\Omega}}\, u$$

where $\underline{\underline{\Omega}} = \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}$

and is connected in a simple way with the operator of angular momentum of the particle. ~~The~~ to one component of this is given by

$$\underline{\underline{P_1}} = \frac{\hbar}{i}\left(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}\right),$$

and the remaining by cyclic permutation. The magnitude of the angular momentum vector is given by

$$\underline{\underline{P^2}} = \underline{\underline{P_1^2}} + \underline{\underline{P_2^2}} + \underline{\underline{P_3^2}}$$

is then simply $\underline{\underline{P^2}} = -\hbar^2\underline{\underline{\Omega}}$.

For the case of the central field the wave equation (123) is separable according to

$$u = f(r)\,Y(\vartheta,\varphi)$$

wherein, with a real number λ,

$$\underline{\underline{\Omega}}\,Y = \lambda Y \qquad (130)$$

and $f(r)$ satisfies the equation

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{d^2}{dr^2}(rf) + \frac{\lambda}{r^2}f\right] + V(r)f = Ef$$

It is now important to determine the solutions of (130) and the eigen-values of $\underline{\underline{\Omega}}$. The answer is well-known. Only for

$$\lambda = -l(l+1)$$

where l is a non-negative integer ($l \geq 0$), there exist solutions of (130) free from singularities, and these are the general spherical harmonics of order l. Of these $2l+1$ are linearly independent. The eigen-values of $\underline{\underline{P^2}}$ are accordingly

$\hbar^2 \cdot l(l+1)$. One can so choose the $Y_l(\vartheta,\phi)$ that the operator

$$\underline{\underline{P_3}} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

multiplies the function $Y_l(\vartheta,\phi)$ simply with its eigen-value. These are then $\hbar m$, where the integer m runs from $-l$ to $+l$

$$Y_{l,m}(\vartheta,\phi) = Y_{l,m}(\vartheta)\, e^{im\varphi}.$$

The $Y_{l,m}$ are orthogonal for the same l but different m as can be directly seen, and for different l as can however be seen from the differential equation. In fact, for two arbitrary functions Y_1 and Y_2

$$\sin\vartheta\left(Y_1 \underline{\underline{\Omega}} Y_2 - Y_2 \underline{\underline{\Omega}} Y_1\right) \equiv \frac{\partial}{\partial\vartheta}\left[\sin\vartheta\left(Y_1\frac{\partial Y_2}{\partial\vartheta} - Y_2\frac{\partial Y_1}{\partial\vartheta}\right)\right] + \frac{\partial}{\partial\phi}\left[\frac{1}{\sin\vartheta}\left(Y_2\frac{\partial Y_1}{\partial\varphi} - Y_1\frac{\partial Y_2}{\partial\varphi}\right)\right]$$

wherefrom, by substituting $Y_{l,m}$ for Y_1; $Y_{l',m'}$ for Y_2, according to (130)

$$\int Y_{l',m'}\, Y_{l,m} \sin\vartheta\, d\vartheta\, d\varphi = 0 \quad \text{for } l \neq l'.$$

In this connection it is interesting to discuss the multiple-valued solutions of (130). For example one can be in doubt as to whether the condition of uniqueness of u is necessary, since it is only the density $\psi^*\psi$ of the general solution $\sum c_n e^{-\frac{i}{\hbar}Et} u_n$ that has a physical significance. When all the u_n's of the considered system are multiplied by the same factor of modulus 1 when going over a certain closed path, $\psi^*\psi$ will still be unique. It is shown however that these multiple valued solutions have also certain such singularities at certain places in their derivatives that the orthogonality of the function-system is not ensured, and hence the self-adjointness of the Hamilton-operator is also spoilt (p. 123). In particular is this the case

for the half-integral spherical harmonics $Y_{l,m}(\vartheta, \varphi)$ in which l as well as m differ from an integer by $1/2$.

The solutions of the differential equation (97*) have this property that by a complete going round of a parallel circle their sign is altered. This however is no basis for excluding these solutions. Besides they have the property that

$$\lim_{\vartheta \to 0} \sin\vartheta \left[Y_{l,m} \frac{\partial}{\partial \vartheta} Y^*_{l',m'} - Y^*_{l',m'} \frac{\partial}{\partial \vartheta} Y_{l,m} \right] = Q(0)$$

not zero, but finite. The similarly defined value $Q(\pi)$ is given by

$$Q(\pi) = (-1)^{l+l'} Q(0)$$

For $l \neq l'$ we see that $Y_{l,m}$ gives rise, for half-integral l and m, a point source at the point $\vartheta = 0$, and a corresponding equally strong negative source (sink) at the point $\vartheta = \pi$, while for odd $l' - l$ no compensation for the sources is determined. According to the criterion on p. 123, such functions are not allowed as eigen-functions. In fact for $l \neq l'$ they are not even orthogonal. Accordingly it follows from a general point of view, not merely as a necessary condition for the uniqueness of the eigen-functions, that in our case the quantum numbers l and m should be integral.

The eigen-functions have an important property which follows immediately from equation (124) for the operator $\underline{\underline{H}}$ when we substitute for u and v two different solutions belonging to different energy values E_n and E_m. We thus confine ourselves to the discrete case, because these relations can be applied directly to eigen-solutions. Then it follows that [Put $v = u_m$, $u = u_n$ in (124)]

$$E_n \int u_m^* u_n \, dq = E_m \int u_n u_m^* \, dq$$

accordingly $\int u_m^* u_n \, dq = 0$ for $E_n \neq E_m$ (131)

[* Here it is assumed that the E are all real. This follows from (124)

$v = u = u_n$, since this relation then transforms to

$$E_n \int u_n^* u_n \, dV = E_n^* \int u_n u_n^* \, dV, \text{ i.e. } E_n^* = E_n \Big]$$

This is called the orthogonality of the eigenfunctions. It is to be mentioned here that for the same energy value E_n several linearly independent Eigenfunctions might exist. The most general solution for this eigen-value has then the form

$$u_n = c_1 u_{n,1} + c_2 u_{n,2} + \cdots + c_g u_{n,g}$$

where $c_1, c_2 \cdots c_g$ are arbitrary constants. Their number g is called the weight of the state is equal to the maximum number of linearly independent solutions which exist for this state. (In the above mentioned example of the hydrogen atom the weight is n^2, for the plane oscillator $n+1$ while the state of the simple harmonic oscillator is simple). We can orthogonalise the basis $u_{n,1}, \cdots u_{n,g}$ of the solutions of (123) for a specified E_n ie with the aid of chosen linear combinations substitute one for another for which the condition (131) is satisfied for all pairs of u_n, u_m different from each other, and we shall assume this in what follows. Since a constant factor is further undetermined in each u_n, we can further normalise this according to $\int u_n^* u_n \, dq = 1$. (131′)

A complex factor of modulus 1 still remains always undetermined in u_n.

We now come up to the question of the possibility of a series development

$$f \sim a_1 u_1 + \cdots + a_n u_n + \cdots \qquad (132)$$

for an arbitrary function f, for which $\int |f|^2 dq$ exists, where

$$a_n = \int f u_n^* \, dq \qquad (133)$$

as can be found by solutions solving with the help of the orthogonality relations (131), (131′). The sign $\sim$ indicates that the series is in general not convergent in the ordinary sense, but only convergent in the mean ie

$$\lim_{N\to\infty} \int \left| f - \sum_{k=1}^{N} a_k u_k \right|^2 dq = 0 \qquad (132')$$

This is specially to be noted when f possesses any quadratic integrable singularities; for the series development to be possible convergence in the mean must hold and can in no way be copied otherwise and conversely. The integral in the relation (132') can be transformed to

$$\int |f|^2 dq - \sum_{k=1}^{N} a_k^* \int f u_k^* dq - \sum_{k=1}^{N} a_k \int f^* u_k \, dq + \sum_{k,l=1}^{N} a_k a_l^* \int u_k u_l^* dq$$

Or in view of (131), (131') and (133) into

$$\int |f|^2 dq - 2 \sum_{k=1}^{N} a_k^* a_k + \sum_{k=1}^{N} a_k a_k^* = \int |f|^2 dq - \sum_{k=1}^{N} a_k^* a_k$$

As a consequence (132') is equivalent to

$$\int |f|^2 dq = \sum_{k=1}^{\infty} a_k^* a_k \qquad (134)$$

whereby at the same time the convergence of the concerned series results. This relation is also called the completeness relation, since it is a criterion in order that no u_n is missing or no new linearly independent function comes in addition. Since the relation between the function f and the coefficients a_n is linear, it follows that for two arbitrary functions

$$f \sim a_1 u_1 + \cdots + a_n u_n + \cdots ; \quad a_n = \int f u_n^* dq$$

$$g \sim b_1 u_1 + \cdots + b_n u_n + \cdots ; \quad b_n = \int g u_n^* dq$$

$$\int f^* g \, dq = \sum_{k=1}^{N} a_k^* b_k ; \text{ accordingly also } \int f g^* dq = \sum_{k=1}^{N} a_k b_k^* \qquad (134')$$

This can be seen from the fact that (133) must also be valid when one substitutes

$\lambda f + \mu g$ for f, (with λ and μ arbitrary numbers), and $\lambda a_k + \mu b_k$ for a_k.

A generalisation of the orthogonality relation (131) is obtained by introducing the elementary wave packet $\bar{u}_{\lambda'\lambda''} = \bar{u}_{\lambda''} - \bar{u}_{\lambda'}$ defined by (126). The application of the relation (124) to these functions gives

$$\int \bar{u}^*_{\lambda_1'\lambda_1''}\ \bar{u}_{\lambda_2'\lambda_2''}\, dq = 0 \quad \text{, when } (\lambda_1'\lambda_1'') \text{ is outside } (\lambda_2'\lambda_2'') \tag{131''}$$

When further we are dealing with a pure continuous spectrum, there exists the limit

$$\lim_{\Delta\lambda \to 0} \frac{1}{\Delta\lambda} \int \bar{u}^*_{\lambda,\lambda+\Delta\lambda}\ \bar{u}_{\lambda,\lambda+d\lambda}\, dq \longrightarrow G(\lambda)$$

accordingly, $$\int \bar{u}^*_{\lambda,\lambda+d\lambda}\ \bar{u}_{\lambda,\lambda+d\lambda}\, dq = \int_{\lambda}^{\lambda+\Delta\lambda} G(\lambda)\, d\lambda \tag{135}$$

we can connect (131'') and (135) together in the equation

$$\int \bar{u}^*_{\lambda_1'\lambda_1''}\ \bar{u}_{\lambda_2'\lambda_2''}\, dq = \int_{\lambda'}^{\lambda''} G(\lambda)\, d\lambda \tag{136}$$

where (λ', λ'') denotes the common part-interval of the intervals $(\lambda_1', \lambda_1'')$ and $(\lambda_2', \lambda_2'')$.

The functions $\bar{u}$ as well as u are said to be normalised with respect to the continuous parameter λ, when the function $G(\lambda)$ in (136) is in special equal to 1.

Then, in particular, we have

$$\int \bar{u}^*_{\lambda_1'\lambda_1''}\ \bar{u}_{\lambda_2'\lambda_2''}\, dq = (\lambda'' - \lambda') \tag{137}$$

Introducing in place of λ a function $\mu = f(\lambda)$ as a new parameter, we obtain for the function normalised with respect to μ

$$\bar{u}_{\mu'\mu''} = \int_{\lambda'}^{\lambda''} \sqrt{\frac{d\mu}{d\lambda}}\, d\bar{u}_{\lambda'\lambda} \tag{137'}$$

or briefly speaking: the eigenfunction u_μ is multiplied by $\sqrt{d\mu/d\lambda}$.

In place of the series development (132) now enters further the integral

$$f \sim \int a_\lambda u_\lambda d\lambda = \int a_\lambda \, d\bar{u}_\lambda \tag{138}$$

whereby

$$a_\lambda G(\lambda) = \int f u_\lambda^* \, dq \tag{139}$$

ie

$$a_\lambda = \int f u_\lambda^* \, dq \tag{139'}$$

in case u_λ is normalised according to (137). The completeness relation reads

$$\lim_{\substack{\lambda_1 \to -\infty \\ \lambda_2 \to +\infty}} \int \left| f - \int_{\lambda_1}^{\lambda_2} a_\lambda u_\lambda \, d\lambda \right|^2 dq = 0 \,, \quad \text{or} \quad \lim_{\substack{\lambda_1 \to -\infty \\ \lambda_2 \to +\infty}} \int \left| f - \int_{\lambda_1}^{\lambda_2} a_\lambda \, d\bar{u}_\lambda \right|^2 dq = 0$$

which, on the basis of the orthogonality relations, is equivalent to

$$\int |f|^2 dq = \int |a_\lambda|^2 d\lambda \tag{140}$$

and when no normalisation is prescribed

$$\int |f|^2 dq = \int |a_\lambda|^2 G(\lambda) \, d\lambda \tag{140'}$$

and for two functions f, g and their coefficients in their expansion eg a_λ, b_λ

$$\int f g^* dq = \int a_\lambda b_\lambda^* G(\lambda) \, d\lambda \tag{140''}$$

We can now so formulate these results as to bring together the discrete and continuous spectrum or as one ~~point~~ might say the point and interval spectrum in a unitary way. Let $\bar{u}_\lambda$ be again a function defined by (126) which might vary discontinuously with λ, and further let us put for the sake of brevity

$$\bar{u}_{\lambda' \lambda''} = u_{\lambda''} - u_{\lambda'} \,,$$

and also when two intervals $(\lambda_1' \, \lambda_1'')$ and $(\lambda_2' \, \lambda_2'')$ appear let those their

common portion (which can evidently also vanish) be denoted as $(\lambda'\lambda'')$. Abandoning normalisation we write the orthogonality relation in the form

$$\int \bar{u}^*_{\lambda_1'\lambda_2''}\, \bar{u}_{\lambda_2'\lambda_2''}\, dq = \bar{G}(\lambda'') - \bar{G}(\lambda') \qquad (136')$$

where $\bar{G}(\lambda)$ is a discontinuously varying function of λ which is nowhere decreasing with increasing λ and always positive. The giving up of normalisation has besides the advantage that we can take better account of degeneracy, because for a determined value of λ, a complete linear aggregate of eigen-functions can appear for $\bar{u}_\lambda$. When we write instead of (139)

$$\int_{\lambda'}^{\lambda''} a_\lambda d\bar{G}(\lambda) = \int f\, \bar{u}^*_{\lambda'\lambda''}\, dq \qquad (139'')$$

we have a relation which is valid for the discrete as well as the continuous spectrum. The completeness relation can then be written as

$$\int |f|^2 dq = \int_{-\infty}^{+\infty} |a_\lambda|^2 d\bar{G}_\lambda \qquad (141)$$

and,

$$\int f g^* dq = \int_{-\infty}^{+\infty} a_\lambda b^*_\lambda\, d\bar{G}_\lambda \qquad (142)$$

Moreover we consider the operator $\underline{\underline{P}}_\lambda$ which operating on the arbitrary function f converts it into the integral as in (138) extract with the upper limit λ i.e.

$$\underline{\underline{P}}_\lambda f = \int_{-\infty}^{\lambda} a_\lambda d\bar{u}_\lambda .$$

This operator is called the projection-operator because it projects the class of a_λ to a subset - namely all those which vanish outside the interval $(-\infty, \lambda)$. Obviously the projection operator $\underline{\underline{P}}$ has the property

$$\underline{\underline{P}}^2 = \underline{\underline{P}} \qquad (143)$$

and conversely we shall call every operator $\underline{\underline{P}}$ with this property as a projection-operator. In our case it follows that for $\lambda'' > \lambda'$ the operator

$$P_{\lambda'\lambda''} \equiv P_{\lambda''} - P_{\lambda'}$$

is equally a projection operator:

$$\left(\underline{\underline{P}}_{\lambda''\lambda'}\right)^2 \equiv \left(\underline{\underline{P}}_{\lambda''} - \underline{\underline{P}}_{\lambda'}\right)^2 = \underline{\underline{P}}_{\lambda''\lambda'} \text{ for all } \lambda'' > \lambda' \qquad (I)$$

further, $P(-\infty) = 0\,; \quad P(+\infty) = 1 \qquad (II)$

for $\lambda' > \lambda$ and $\lim \lambda' \to \lambda$, $P_{\lambda'} \to P_\lambda$

Next we shall search for the relation between the operators $\underline{\underline{H}}$ and $\underline{\underline{P}}_\lambda$. According to (123') one has

$$\underline{\underline{H}}\, \bar{u}_{\lambda'\lambda''} = \int_{\lambda'}^{\lambda''} E(\lambda)\, d\bar{u}_\lambda$$

and hence

$$\underline{\underline{P}}_{\lambda'\lambda''} f = \int_{\lambda'}^{\lambda''} a_\lambda\, d\bar{u}_\lambda \;;\; \underline{\underline{H}}\,\underline{\underline{P}}_{\lambda'\lambda''} f = \int_{\lambda'}^{\lambda''} a_\lambda E_\lambda\, d\bar{u}_\lambda = \int_{\lambda'}^{\lambda''} E(\lambda)\, d\left(\underline{\underline{P}}_{\lambda'\lambda''} f\right). \qquad (144)$$

For $\lambda' \to -\infty$, $\lambda'' \to +\infty$, this goes over to

$$\underline{\underline{H}} f = \int_{-\infty}^{+\infty} E(\lambda)\, d\left(\underline{\underline{P}}_\lambda f\right) \qquad (III)$$

which means the same as: for all g one has

$$\int (g^* \underline{\underline{H}} f)\, dq = \int_{-\infty}^{+\infty} E(\lambda)\, d\left(\int g^* \underline{\underline{P}}_\lambda f\, dq\right) \qquad (III')$$

Instead of arbitrary parameters λ we have here introduced the energy itself. The eigen-value problem is defined in a very general way by the conditions (I), (II) and (III). As to the question of its solvability we

we shall speak about it in the next article.

For calculations it is often useful to introduce the integral

$$\int u_\lambda^* u_\lambda \, dq$$

as an improper form. Let $\delta(\lambda)$ be an improper function with the property that for for ~~co~~ all continuous

$$\int_{\lambda_1}^{\lambda_2} f(\lambda)\,\delta(\lambda)\,d\lambda = \begin{cases} f(0) \\ 0 \end{cases} \text{ when } 0 \text{ lies } \begin{cases} \text{in} \\ \text{outside} \end{cases} (\lambda_1, \lambda_2) \qquad (145)$$

so that

$$\int u_\lambda^* u_{\lambda'}^{\varphi} dq = G(\lambda)\,\delta(\lambda'-\lambda) \text{ or } = \delta(\lambda'-\lambda) \qquad (146)$$

Later on, we shall also be using the derivative δ' of the δ-function which is defined by

$$\int_{\lambda_1}^{\lambda_2} f(\lambda)\,\delta'(\lambda)\,d\lambda = -\int_{\lambda_1}^{\lambda_2} f'(\lambda)\,\delta(\lambda)\,d\lambda = \begin{cases} -f'(0) \\ 0 \end{cases} \text{ when } 0 \text{ lies } \begin{cases} \text{inside} \\ \text{outside} \end{cases} (\lambda_1, \lambda_2) \;..\; (147)$$

These relations are to be considered as formally useful abbreviations of (136), (137).

As regards the general differential equation (123) of the eigen-value problem it is to be remarked that it is always equivalent to a variation problem

$$\delta \int u^* (\underline{\underline{H}} u)\, dq = \delta \int (\underline{\underline{H}} u)^* u \, dq = 0 \qquad (148)$$

with the subsidiary condition

$$\int u^* u \, dq = 1 \qquad (149)$$

Here u and u^* are to be varied independently of each other. Under certain circumstances, (148) can be transformed by integration by parts - for eg in the case

Cartesian coordinates and the Hamiltonfunction

$$\underline{\underline{H}} = -\sum_k \frac{\hbar^2}{2m_k}\left(\frac{\partial}{\partial q_k} - \frac{ie_k}{\hbar c}\Phi_k\right)^2 + V(q)$$

into $$\delta\int\left[\sum_k \frac{\hbar^2}{2m_k}\left(\frac{\partial u^*}{\partial q_k} + \frac{ie_k}{\hbar c}\bar{\Phi}_k\right)\left(\frac{\partial u}{\partial q_k} - \frac{ie_k}{\hbar c}\Phi_k\right) + Vu^*u\right]dq = 0 \qquad (150)$$

with the subsidiary condition (149). The value of (~~150~~) the integral (150) is on account of (123) exactly equal to the energy value. This variation problem is often useful for the ~~approximate~~ integration of the differential equation by successive approximations, because the function u may have special forms, and the additional conditions aid the solution of the problem. Thereby one finds the value of the variation integral always greater than the true eigen-value.

Two general theorems can be further mentioned. In the case of real eigen-functions, when they exist, the eigenfunctions without "Knotenzahlen" (zeroes) belong to the least eigen-value. For real eigen-functions of a single variable the order of increasing zeroes of eigenfunctions corresponds to the order of increasing eigenvalues. The "Knotenzahl" appears then as the "quantum number" of the system.

(7). General transformations of operators and matrices: with the help of the completeness relation we can construct an important relation between the operators working on u_n and matrices corresponding to them. Let $\underline{F}$ be a linear operator, then there corresponds to every eigen-function u_n a development

$$(\underline{\underline{F}}\, u_n) \sim \sum u_K F_{Kn} \quad \text{with} \quad F_{Kn} = \int u_K^* (\underline{\underline{F}}\, u_n)\, dq \tag{151}$$

If $\underline{\underline{F}}$ be hermitian, one has

$$\int u_K^* (\underline{\underline{F}}\, u_n)\, dq = \int (\underline{\underline{F}}\, u_K)^* u_n\, dq$$

ie
$$F_{Kn} = (F_{nK})^* \tag{152}$$

ie the matrix is therefore accordingly hermitian. We now consider two hermitian operators

$$\underline{\underline{F}}\, u_n \sim \sum u_K F_{Kn} \; ; \qquad F_{Kn} = \int u_K^* (\underline{\underline{F}}\, u_n)\, dq$$

$$\underline{\underline{G}}\, u_m \sim \sum u_K G_{Km} \; ; \qquad G_{Km} = \int u_K^* (\underline{\underline{G}}\, u_m)\, dq .$$

Applying now the completeness relation (134') (which is valid for all n, m) we have

$$\int (\underline{\underline{F}}\, u_n)^* (\underline{\underline{G}}\, u_m)\, dq = \sum_{K=1}^{\infty} F_{Kn}^* G_{Km}$$

and by application of the hermiticity of $\underline{\underline{F}}$

$$\int u_n^* (FG\, u_m)\, dq = \sum_K F_{nK} G_{Km} \tag{153}$$

On the basis of (151) there corresponds a matrix to every operator, and if the operator be hermitian the matrix is hermitian. From (153) it then follows that

To the product of two matrices $\underline{\underline{F}} \cdot \underline{\underline{G}}$ corresponds the product of the matrices $(F) \cdot (G)$ which is formed according to the usual rule for multiplication of matrices. This last rule reads

$$(FG)_{nm} = \sum_K F_{nK} G_{Km} \tag{153'}$$

It is to be observed that we assume here only the hermiticity of $\underline{\underline{F}}$ and $\underline{\underline{G}}$ and not that of $(\underline{\underline{F}} \cdot \underline{\underline{G}})$ and also no assumption is made of $\underline{\underline{F}}$ and $\underline{\underline{G}}$ being

commutative.

If the development $\sum_k a_k u_k$ belongs to an arbitrary function f, then to the function $\underline{F} f$ belongs the development $\sum_k (\underline{F} u_k) a_k = \sum_{l,k} u_l F_{lk} a_k$.

[Strictly speaking it is to be shown that this statement is fulfilled for convergence in the mean. Let us the denote the Nth partial sum $\sum_1^N a_k u_k$ by f_N, so that

$$\lim_{N\to\infty} \int |f - f_N|^2 dq = 0$$

We now require of the operator $\underline{F}$ the following property: Corresponding to $\underline{F} f_N = g_N$ there is a g such that $\lim_{N\to\infty} \int |g - g_N|^2 dq = 0$, and $\underline{F} f = g$ holds. Accordingly two functions g and g' for which $\int |g - g'|^2 dq = 0$ are not to be considered fundamentally different. In our case the existence of such a g is assured when the sum $\sum_1^\infty |b_k|^2$ converges ($b_k = \sum_l F_{kl} a_l$), and this is further the case when for all k, the sum

$$\sum_l |F_{kl}|^2 = \sum_l |F_{lk}|^2$$

converges.]. Accordingly we can set up the coefficients $(b_1, b_2, \ldots b_n, \ldots)$ as corresponding to the coefficients $(a_1, a_2, \ldots a_n, \ldots)$ by means of a $\underline{F}$ such that

$$b_n = \sum_m F_{nm} a_m \qquad (154)$$

Thus the matrix equivalent to the operator $\underline{F}$ determines a linear manifold in the infinitely many-dimensional vector space of the coefficients in the development (a) of our function system. The hermiticity of $\underline{F}$ is expressed by the fact that

$$\sum_n a_n^* b_n = \sum_n a_n b_n^* \qquad (155)$$

ie the "scalar product" is accordingly real.

In the general expression (151) for the matrix element F_{kn} is contained the fact that for the diagonal element

$$F_{nn} = \int u_n^* (\underline{\underline{F}}\, u_n)\, dq \qquad (156)$$

we have seen in previous articles that, in simple cases, this expression has the significance of a mean value or expectation value. We have there started from the expression $|\varphi(p)|^2 dp$ as the probability that the momentum p of the concerned state of the system lies between p and $p+dp$. Then for the mean value of an arbitrary rational function of p & we have

$$\int F(p)\, |\varphi(p)|^2 dp = \int \psi^*(q) \left\{ \underline{\underline{F}} \left(\frac{\hbar}{i} \frac{\partial}{\partial q} \right) \psi(q) \right\} dq .$$

Equally for an arbitrary function F of q

$$\overline{F} = \int \psi^* (F \psi)\, dq$$

whereas which further corresponds with (156) when by $\underline{\underline{F}}$ one means simply multiplication with q. Finally if one has a function F which is linear in p but arbitrary in q,

$$F = \frac{1}{2} \sum_K \left[A_K(q)\, p_K + p_K\, A_K(q) \right]$$

(the symmetrising being to ensure hermiticity), we can introduce for the case of cartesian coordinates the current density i_K and obtain

$$\overline{F} = \sum_K \int A_K(q) \left[m i_K + \frac{e}{c} \Phi_K \right] dV = \sum_K \int \psi^* \frac{1}{2} \left[A_K \frac{\hbar}{i} \frac{\partial \psi}{\partial q_K} + \frac{\hbar}{i} \frac{\partial}{\partial q_K} (A_K \psi) \right] dq$$

Since further the expectation value of the sum of two magnitudes is the sum of the expectation values, and (156) is linear in the operator F, we can consider (156) to be valid for operators which are sums of the types considered. In particular it is valid when we introduce the Hamiltonian $\underline{\underline{H}}$ in place of the operator $\underline{\underline{F}}$.

For such operators F, which in this sense correspond to physical magnitudes - ie properties of the system which can be described by specifying numerical values which can be determined in principle by experimental arrangements (ie measures), we might say that the diagonal element F_{nn} is equal to the expectation value of the corresponding magnitude F for the state of the system characterized by the eigen-value function U_n. As to what the physical magnitudes are which of a system are and how they are to be measured can only be distinguished when one builds up a theory on the basis of the results of experiments. [This standpoint is different from the one according to which, every hermitian operator corresponds to a magnitude or "observable" of the system, and has always a direct physical sense in that one can speak of the probability that the magnitude F has a determinate value for the concerned state] We remark further that for these special operators $\underline{\underline{F}}$, only the diagonal elements of the matrix F contain a direct physical meaning.

The non-diagonal elements can only be indirectly connected with the data of measurements, in the following way: The mean value of an arbitrary rational function $f(F)$ of the operator $\underline{F}$, in particular any powers of F, is given or defined by the diagonal element $[f(F)]_{nn}$ of $f(F)$. If one uses formally the multiplication law of matrices for building up of $[f(F)]_{nn}$, one can show that by specifying $[f(F)]_{nn}$ the non-diagonal elements F_{nm} of F can in general be determined uniquely.

For the general relation (151) expressing the connection between matrices and operators it is only assumed that the functions $u_1, u_2, \ldots u_n \ldots$ form a complete orthogonal system. It is useful to investigate how the matrices alter when one goes over to a new system $v_1, v_2 \ldots v_n, \ldots$ which also possesses completeness and orthogonality. First of all there corresponds to every function v_m a development

$$\underline{\underline{S}}\, u_m = v_m = \sum_{(n)} u_n S_{nm} \quad \text{with} \quad S_{nm} = \int u_n^* \left[\underline{\underline{S}}\, u_m\right] dq = \int u_n^* v_m\, dq. \qquad (157)$$

The matrix S_{nm} ~~indefinite~~ defines a linear operator $\underline{\underline{S}}$ which relates every function $f = a_1 \cdot u_1 + a_2 \cdot u_2 + \ldots$ to the function $g = a_1 v_1 + a_2 v_2 + \ldots$ with the same coefficients of expansion in the new system. This $\underline{\underline{S}}$ has accordingly the property

$$\int f u_n^* dq = \int \left[\underline{\underline{S}} f\right] v_n^* dq$$

for all f. This operator $\underline{\underline{S}}$ is however fundamentally of a different sort from the previously concerned hermitian operator $\underline{F}$ which corresponds

to physical magnitudes. We call $\underline{\underline{S}}$ a transformation-operator. Since we have according to the completeness relation

$$\int v_n^* v_m \, dq = \sum_K S_{Kn}^* S_{Km}$$

the orthogonality and completeness of the v_n is expressed by

$$\sum_K S_{Kn}^* S_{Km} = \begin{cases} 0 & \text{for } n \neq m \\ 1 & \text{for } n = m \end{cases} \qquad (158)$$

Since from $f \sim \sum a_K u_K$; $g \sim \sum a_K v_K$ it follows that $\sum_K |a_K|^2 = \int |f|^2 dq = \int |g|^2 dq$, and this is equivalent to the condition that for all f one has

$$\int |\underline{\underline{S}} f|^2 dq = \int |f|^2 dq \qquad (159)$$

and for two arbitrary f and g

$$\int (\underline{\underline{S}} f)^* (\underline{\underline{S}} g) \, dq = \int f^* g \, dq \qquad (159')$$

The operator $\underline{\underline{S}}$ is accordingly not hermitian but has, according to (159) the property of "length-invariance" when we use $\int |f|^2 dq$ as the measure of the "length" of a function, and more generally $\int |f-g|^2 dq$ as that of the "distance" between two functions. Since further the $v_n = (\underline{\underline{S}} u_n)$ form a complete function system, the totality of $\underline{\underline{S}} f$ must correspond to any f. ie there must exist for all f also an inv operator S^{-1} inverse to S. The completeness of the system of v simultaneously means that the u_n must be capable of being expanded in terms of v_n's according to

$$u_m \approx \sum_{(n)} v_n S^{-1}_{nm} \; ; \; S^{-1}_{nm} = \int v_n^* \left[\underline{\underline{S}}^{-1} v_m \right] dq = \int v_n^* u_m dq \qquad (157')$$

and comparison with (157) gives

$$S^{-1}_{nm} = S^*_{nn} \qquad (160)$$

Thus (S) is not a hermitician matrix, but the hermitician-conjugate of S viz $\underline{\underline{\tilde{S}}}$ (ie the one obtained from $\underline{\underline{S}}$ by taking the conjugate-complex and interchanging rows and columns) is identical with the reciprocal matrix S^{-1} of S:

$$S^{-1} = \tilde{S} \qquad (161)$$

In fact, on account of $S^*_{kn} = \tilde{S}_{nk}$, (158) is equivalent to

$$\tilde{S} S = I \qquad (158')$$

where I signifies the unit matrix. The completeness of the function system v_n signifies, as follows from (157') by application of the completeness relation, that also

$$\sum_K \left(S^{-1}_{kn} \right)^* S^{-1}_{Km} = \begin{cases} 0 & \text{for } n \neq m \\ 1 & \text{for } n = m \end{cases} \qquad (162)$$

or according to (160)

$$\sum_K S_{nK} S^*_{mK} = \begin{cases} 0 & \text{for } n \neq m \\ 1 & \text{for } n = m \end{cases} \qquad (163)$$

which in matrix method of writing becomes

$$S \tilde{S} = I \qquad (163')$$

It is important to emphasise that (163') is not a consequence of (158') but follows from (158') when and only when there exists an operator $\underline{\underline{S}}^{-1}$ An operator S is called unitary when

it has besides the property of length-invariance (eqn 159) the property of the existence of a reciprocal operator without an exception: corresponding a matrix S is called unitary when it satisfies both the relations (158') and (163'). The transformation-operators are such unitary operators. By putting together (multiplication) of two unitary operators (matrices) there results again an unitary operator (a unitary matrix).

It is perhaps useful to emphasise the analogues of these relations in the case of magnitudes which are capable of taking on only a finite number of values, say N. In this case the complete function-system consists of N orthogonal (complex) vectors $u_k(1), u_k(2), \ldots u_k(N)$ where instead of q the values $q_1 \ldots q_N$ of the corresponding magnitudes are put in. An orthogonal system of vectors in a finite dimensional space is complete when and only when the number p of vectors coincides with the dimensional number N of the system. The case of matrix S, for which

$$\tilde{S}\,S = 1$$

while $S\tilde{S} \neq 1$ appears when S is not a quadratic matrix but a rectangular matrix S_{nm} $(n = 1, 2 \ldots N;\ m = 1, 2, \ldots p)$ in which the number of columns is less than the number of rows. It is clear then that $S\tilde{S}$ is not the unit matrix, and the reciprocal $\underline{\underline{S}}^{-1}$ of the transformation $\underline{\underline{S}}$, which transforms the vector $f(r) = \sum_{k=1}^{N} a_k u_k(r)$; $r = 1, \ldots N$ into $\left[\underline{\underline{S}}\, f(r)\right] = \sum_{i=1}^{p} a_i v_i(r)$, exists for all $f(r)$ when and only when $p = N$. The condition that $S\tilde{S} = I$

be valid along with $\tilde{S}S = I$ is here equivalent to $\underline{S}$ being a quadratic matrix. For matrices $\underline{S}$ with infinitely many columns and rows the completeness cannot however be determined by such enumeration, and hence arises the necessity of assuming the existence without exception of the reciprocal as a new condition besides the relation $\tilde{S}S = I$.

We can now answer the question as to how the matrix F corresponding to the operator $\underline{\underline{F}}$ according to (151) changes when the function system is transformed from u_K to v_K. We have according to (157)

$$\left.\begin{aligned} F'_{nm} &= \int v_n^* \left(\underline{\underline{F}}\, v_m\right) dq \\ F'_{nm} &= \sum_K \sum_l \int S^*_{Kn}\, u_K^*\, S_{lm}\, \underline{\underline{F}}(u_l)\, dq \end{aligned}\right\} \qquad (151')$$

accordingly because,

$$\left.\begin{aligned} F_{Kl} &= \int u_K^*\, \underline{\underline{F}}(u_l)\, dq \\ \text{one has,}\quad F'_{nm} &= \sum_{K,l} S^*_{Kn}\, F_{Kl}\, S_{lm} \end{aligned}\right\} \qquad (164)$$

[Convergence questions here are very complicated]

or in matrix notation,

$$(F') = \tilde{S}FS = S^{-1}FS \qquad (164')$$

which admits the converse

$$(F) = SF'S^{-1} = SF'\tilde{S} \qquad (164'')$$

One could verify easily that $\underline{\underline{F}}'$ is again a Hermitian matrix if $\underline{\underline{F}}$ be one. $\left[\; F'^*_{nm} = \sum S_{Kn}\, F^*_{Kl}\, S^*_{lm} = \sum S_{Kn}\, F_{lK}\, \tilde{S}_{ml} = \sum \tilde{S}_{ml}\, F_{lK}\, S_{Kn} = F_{mn} \;\right]$

In the operator notation (164) signifies: when $\underline{\underline{F}}$ transforms the function f into the function g, $\underline{\underline{F}}'$ transforms $\underline{\underline{S}} f$ into $\underline{\underline{S}} g$.

[Let $f = \sum a_K u_K$; $\underline{\underline{S}} f = \sum_{K,n} a_K v_n S^{-1}_{nK}$; $\underline{\underline{F}}' \underline{\underline{S}} f = \sum_{l,K,n} a_K S^{-1}_{nK} F'_{ln} v_l$

$g = \underline{\underline{F}} f = \sum_{K,l} a_K u_l F_{lK}$; $Sg = \sum_{K,l,n} a_K F_{lK} v_n S^{-1}_{nl} = \sum_{K,l,n} a_K F_{nK} v_l S^{-1}_{ln}$

and $S^{-1}_{nK} F'_{ln} = F_{nK} S^{-1}_{ln}$ ie $F'_{ln} S^{-1}_{nK} = S^{-1}_{ln} F_{nK}$ means

$F' S^{-1} = S^{-1} F$ or $F' = S^{-1} F S$]

In this representation the coordinate system of the $u_1 \ldots u_n$ is kept fixed and the operator varied, while we could go from this to keeping the operator fixed, and varying the coordinate system.

The fundamental V-R (103) for the operators $\underline{\underline{p}}_k$, $\underline{\underline{q}}_l$ go over plainly into the corresponding matrix equations, when we substitute for the functions f on which these operators act the sequence of their coefficients $a_1 \ldots a_n \ldots$ in the development in an arbitrarily complete orthogonal system $v_1, v_2 \ldots v_n \ldots$

[For eg. let $\underline{\underline{p}}_r \underline{\underline{q}}_r = \underline{\underline{F}}_1$, and $\underline{\underline{q}}_r \underline{\underline{p}}_r = F_2$. The V-R is $\underline{\underline{F}}_1 f - \underline{\underline{F}}_2 f = \frac{\hbar}{i} f$

By the transformation this becomes $\underline{\underline{S}}\,\underline{\underline{F}}_1 f - \underline{\underline{S}}\,\underline{\underline{F}}_2 f = \frac{\hbar}{i} \underline{\underline{S}} f$

or from the above $\underline{\underline{F}}_1' \underline{\underline{S}} f - \underline{\underline{F}}_2' \underline{\underline{S}} f = \frac{\hbar}{i} \underline{\underline{S}} f$

giving rise to the transformed V-R, $F_1' - F_2' = \hbar/i$]

In fact these V-R are plainly invariant under arbitrary unitary transformations

of the form (164).

Now we can characterise very simply the special eigenfunctions $u_1, u_2 \ldots$ which satisfy the equation

$$\underline{\underline{H}}\, u = E u$$

and correspond to the stationary states of our system with the Hamiltonian operator $\underline{\underline{H}}$. There are certain orthogonal and normalised functions u, for which the matrix of the Hamiltonfunction (Energy) would be

$$(H_{nm}) = \int u_n^* \, (\underline{\underline{H}}\, u_m)\, dq$$

would be a diagonal matrix

$$H_{nm} = \begin{cases} 0 & \text{for } n \neq m \\ E_n & \text{for } n = m \end{cases} \qquad (165)$$

With the help of this result we can formulate the problem of determining the eigen-values E_n of the energy and the matrices $p_{nm}^{(k)}$, $q_{nm}^{(k)}$ without a knowledge of the wave equation. We write first the V-R with the help of the rule of matrix multiplication so that the condition that the diag energy matrix be diagonal is expressed in terms of the matrix-elements of $p^{(k)}$ and $q^{(k)}$ by with the help of the same rule. One obtains in this manner infinitely many equations to determine the matrix elements of p and q as well as the eigen-values of the energy. This was the theorem of Heisenberg's "matrix-mechanics" which historically was discovered before the representation by the wave-equation. The practical solution of these equations is achieved only in few cases, for. Eg. for the

harmonic oscillator. In the case of the Hydrogen atom the determination of energy values is however possible but the determination of the matrix elements of p and q themselves is no longer achieved. This is connected with the fact that here the continuous spectrum also appears, in which case the matrix-calculation becomes very complicated. We shall come back to this point very soon. On the other hand the matrix method is often useful when one deals with a sub-space of a finite dimensional number. Such a sub-space appears for example in the case of degenerate systems ie when to a determinate eigen-value many, say g, states correspond. In this case one can prescribe ~~specify~~ inside this subspace an arbitrary unitary transformation according to (164) without interfering with the system of equations to be solved, since in this sub-space the energy-matrix is equal to the unit matrix multiplied by the fixed number E which remains invariant under the considered transformation. In wave mechanics this corresponds to the possibility of transforming the eigenfunctions $u_1 \dots u_g$ considered normal & orthogonal and belonging to E according to

$$u'_m = \sum_{n=1}^{g} u_n S_{nm} \qquad (m = 1, 2 \dots g)$$

Here S is a special unitary g-rowed (quadratic) matrix, so that the orthogonality of the function system remains invariant under the transformation. In the matrix picture the Eigenwert problem can further be formulated in a slightly different way. We take for p_i, q_k matrices

any matrices which satisfy the V-R (wave mechanically these might correspond to a certain orthogonal function system). By application of the multiplication rule of matrices we obtain for the energy a certain Hermitian matrix H_{mn}. The problem now is to bring this unitarily to the diagonal form ie to solve for each possible E the infinitely many linear equations

$$\underline{\underline{S}}^{-1}\,\underline{\underline{H}}\,\underline{\underline{S}} = E$$

or
$$\underline{\underline{H}}\,\underline{\underline{S}} = \underline{\underline{S}}\,\underline{\underline{E}} \;;\; \sum_m H_{nm} S_m = S_n E \qquad (166)$$

[$\sum H_{nm} S_{mK} = \sum S_{nm} E_{mK} = S_{nK} E_{KK}$

$E_{KK} = E_K$ which is here merely denoted by E.

Thus S_n and S_m might be taken as elements corresponding to E_K or the elements of the Kth column (or row) of matrix S. Thus the above equation can be written $\sum H_{nm} S_m = S_n E$]

The condition that $\underline{\underline{S}}$ be unitary demands the normalisation condition

$$\sum |S_n|^2 = 1 \qquad (166')$$

for the coefficients.

[$S\tilde{S} = 1$ gives $\sum S_{nK} \tilde{S}_{Km} = \delta_{nm}$ ie $\sum_K S_{nK} S^*_{mK} = \delta_{nm}$

or in the notation of (166) $\sum_K S_n S_n^* = 1$ which is (166')]

For every possible value E_ρ of E one thus obtains the system of coefficients $S_{n\rho}$

[Infact equation (166) might be considered as defining S_m only, and the connection with the matrix S_{nm} is here established]

and it is easy to see that on the basis of (166') itself it would be unitary, if $\underline{H}$ be hermitian.

[(166') gives $S\tilde{S} = 1$, and from $\underline{\tilde{S}}^{-1}\underline{H}\underline{S} = \underline{E}$, $\tilde{S}^{-1}\tilde{H}\tilde{S} = E$ ie $\tilde{S}^{-1}H\tilde{S} = E$.

ie $SHS^{-1} = E$ giving $\tilde{S}S = 1$]

Also the system of equations is, in general, not solvable but we shall however that it can be practically applied in perturbation theory.

We shall now announce the generalisation of these results for the continuous spectrum, without taking into consideration convergence questions. If the eigen-functions be normalised with respect to the parameter λ or the parameters $\lambda_1 \ldots$, we can form analogous to (151)

$$\underline{F}\, u_\lambda \sim \int u_{\lambda'} F_{\lambda'\lambda}\, d\lambda' \; ; \qquad F_{\lambda'\lambda} = \int u^*_{\lambda'} (\underline{F}\, u_\lambda)\, dq \qquad (151')$$

In the $F_{\lambda'\lambda}$ and even in u itself might appear the δ-symbols defined by (145) and (147) might be made to appear. For eg. we can choose for λ the numerical value of q and for u choose the δ-function $u_{q'}(q) = \delta(q - q')$ where $\delta(q - q')$ stands as the abbreviation for $\delta(q_1 - q_1')\,\delta(q_2 - q_2') \ldots \delta(q_f - q_f')$. Then because of

$$\int u^*_{q'}(q)\, u_{q''}(q)\, dq = \int \delta(q - q')\,\delta(q - q'')\, dq = \delta(q' - q'') \quad [\because (146)]$$

the matrix of q would be

$$\underline{q}_K(q'q'') = \int \delta(q - q')\, q_K\, \delta(q - q'')\, \delta q$$

or $\underline{\underline{q}}_k(q', q'') = q_k' \, \delta(q' - q'')$ (167)

[because of $\int f(\lambda)\, \delta\lambda \, d\lambda = f(0)$ or $\int f(q)\, \delta(q - q')\, dq = f(q')$]

Also, $\underline{\underline{p}}_k(q', q'') = \int \delta(q - q') \frac{\hbar}{i} \frac{\partial}{\partial q_k} \delta(q - q'')\, dq$

or $\underline{\underline{p}}_k(q', q'') = \frac{\hbar}{i} \delta_k'(q' - q'')$ (167')

where the last expression is the abbreviation for

$$\delta(q_1' - q_1'') \cdots \delta(q_{k-1}' - q_{k-1}'')\, \delta'(q_k' - q_k'')\, \delta(q_{k+1}' - q_{k+1}'') \cdots \delta(q_f' - q_f'').$$

[(167') follows from $\int f(q)\, \delta'(q - q')\, dq = -\int f'(q)\, \delta(q - q')\, dq = -f'(q')$]

We can confirm the formal validity of

$$\int \left[\underline{\underline{p}}_k(q', q''') \underline{\underline{q}}_k(q''', q'') - \underline{\underline{q}}_k(q', q''') \underline{\underline{p}}_k(q''', q'') \right] dq''' = \frac{\hbar}{i} \delta(q' - q'')$$

[$\int \underline{\underline{p}}_k(q', q''') \underline{\underline{q}}_k(q''', q'')\, dq''' = \frac{\hbar}{i} \int \delta_k'(q' - q''')\, q_k'''\, \delta(q''' - q'')\, dq'''$

$= \frac{\hbar}{i} \int \delta(q_1' - q_1''') \cdots \delta'(q_k' - q_k''') \cdots q_k'''\, \delta(q''' - q'')\, dq_1''' \cdots dq_k''' \cdots$

$= \frac{\hbar}{i} \int \delta(q' - q''')\, \delta(q''' - q'')\, dq'''$ (using (167'))

$= \frac{\hbar}{i} \delta'(q' - q'')$. The other part of the integral vanishes since there appears $\delta'(q''' - q'')$ while $\underline{\underline{q}}_{ik}$ gives $q_k' \, \delta(q_k' - q''')$.]

[P.T.O]

In reality all these symbols have a meaning when they are multiplied by arbitrary functions f^* and g of q' and q'' and integrated, for eg

$$\int_{q_1'}^{q_2'} \int_{q_1''}^{q_2''} f^*(q')\, \underline{\underline{q}}_k(q', q'')\, g(q'')\, dq'\, dq'' = \int_{q_1}^{q_2} f^*(q)\, q_k\, g(q)\, dq$$

$$= \delta(q_1 - q_1'')\,\delta(q_2' - q_2'') \cdots \int \delta'(q_K' - q_K''')\, q_K'''\, \delta(q_K''' - q_K'')\, dq_K'''$$

Similarly $\underline{\underline{q_K}}\,\underline{\underline{p_K}}$ term gives the expn (without k/i)

$$= \delta(q_1' - q_1'')\,\delta(q_2' - q_2'') \cdots \int q_K'\, \delta(q' - q''')\, \delta'(q''' - q'')\, dq'''$$

Thus one has to evaluate

$$\int \delta'(a-x)\, x\, \delta(x-b)\, dx - \int a\, \delta(a-x)\, \delta'(x-b)\, dx$$

$$= \frac{d}{dx}\Big[x\,\delta(x-b)\Big]_{x=a} - \Big[a\,\delta'(x-b)\Big]_{x=a}$$

$$= a\,\delta'(a-b) + \delta(a-b) - a\,\delta'(a-b) = \delta(a-b) = \delta(q_K' - q_K'')$$

This gives the result.

where (q_1, q_2) is the interval common to (q_1', q_2') and (q_1'', q_2'')

Also analogous to (157) we have the formulae of transformation from one complete system u_λ to another v_μ according to

$$v(\mu; q) = \int u(\lambda; q) S(\lambda, \mu)\, d\lambda$$

with $$S(\lambda; \mu) = \int u^*(\lambda; q)\, v(\mu; q)\, dq \qquad (157')$$

where $S(\lambda, \mu)$ is a unitary matrix which, analogous to (158) and (163), satisfies the relations

$$\int S^*(\lambda, \mu)\, S(\lambda, \mu')\, d\lambda = \delta(\mu - \mu') \qquad (158'')$$

$$\int S(\lambda, \mu)\, S^*(\lambda', \mu)\, d\mu = \delta(\lambda' - \lambda) \qquad (163'')$$

The transformation formulae analogous to (164) are

$$F(\mu; \mu') = \int S^*(\lambda, \mu)\, F(\lambda, \lambda')\, S(\lambda', \mu')\, d\lambda\, d\lambda' \qquad (164')$$

Of special interest is the case where one index is discretely in nrees and the other continuous. we then have

$$v_n(q) = \int u(\lambda; q)\, S_n(\lambda)\, d\lambda\,; \qquad u(\lambda; q) = \sum_n v_n^*(q)\, S_n^*(\lambda) \qquad (168)$$

$$S_n(\lambda) = \int u^*(\lambda; q)\, v_n(q)\, dq \qquad (169)$$

$$\int S_n^*(\lambda)\, S_m(\lambda)\, d\lambda = \delta_{n,m}\,; \quad \sum_n S_n(\lambda) S_n^*(\lambda') = \delta(\lambda - \lambda') \qquad (170)$$

$$F_{n,m} = \int S_n^*(\lambda)\, F(\lambda, \lambda')\, S_m(\lambda')\, d\lambda\, d\lambda'\,; \quad F(\lambda, \lambda') = \sum_{n,m} S_n(\lambda)\, F_{n,m}\, S_m^*(\lambda') \qquad (171)$$

These forms become specially simple when we substitute for the $u(\lambda, q)$ the special system $u_{q'}(q) = \delta(q - q')$. we have then easily

$$S_n(q') = \int \delta(q-q')\, v_n(q)\, dq = v_n(q') \qquad (169')$$

$$\int v_n^*(q)\, v_m(q)\, dq = \delta_{n,m} \; ; \quad \sum_n v_n(q)\, v_n^*(q') = \delta(q-q') \qquad (170')$$

$$F_{nm} = \int v_n^*(q)\, F(q,q')\, v_m(q')\, dq\, dq' \; ; \quad F(q,q') = \sum_{n,m} v_n(q)\, F_{n,m}\, v_m^*(q') \qquad (171')$$

we obtain the important result that the eigen-functions $v_n(q)$ themselves appear as the transformation functions from $\delta(q-q')$ to $v_n(q)$ themselves. If we choose for $v_n(q)$ such $u_n(q)$'s as bring a determinate Hamiltonian operator $\underline{\underline{H}}$ to the diagonal form $H_{nm} = E_n \delta_{nm}$, we might say that the $u_n(q)$ are the transformation functions of the operator $\underline{\underline{q}}$ to the operator $\underline{\underline{H}}$. Then $\underline{\underline{q}}$ and $\underline{\underline{H}}$ would be brought to the diagonal form through the systems $\delta(q-q')$ and $u_n(q)$. As far as relation (170') is concerned, the second one in it is only another symbolic expression for the completeness relation. By integration we obtain for two arbitrary functions f, g, the "actual" relation (non-symbolic)

$$\sum_n \int f^*(q)\, v_n(q)\, dq \int g(q)\, v_n^*(q')\, dq' = \int f^* g\, dq$$

which exactly corresponds to the completeness relation (134'). In particular is this true when f and g are equal to 1 inside a certain region (not necessarily the same for both) and vanish outside it.

(8) The general form of the equations of motion: While we have introduced as the basis of matrix mechanics the ~~pass~~ rule that the

energy matrix be reduced to the diagonal form

$$H_{nm} = E_n \delta_{nm} \tag{165}$$

besides the exchange relations, Heisenberg has made a further prescription which concerns the ~~dependence of~~ dependence of the matrix elements on time. He assumes that the matrix element of every magnitude which does not contain the time explicitly is given ~~so far~~, in so far as its time-dependence is concerned, by

$$F_{n,m}(t) = F_{nm}(0)\, e^{\frac{i}{\hbar}(E_n - E_m)t} \tag{172}$$

or introducing the unitary diagonal matrix

$$U_{n,m}(t) = \delta_{n,m}\, e^{\frac{i}{\hbar} E_n t} \tag{173}$$

$$\underline{\underline{F}}(t) = \underline{\underline{U}}(t)\, \underline{\underline{F}}(0)\, \underline{\underline{U}}^{-1}(t) = \underline{\underline{U}}(t)\, \underline{\underline{F}}(0)\, \underline{\underline{\tilde{U}}}(t) \tag{174}$$

In case the Hamiltonian does not contain the time explicitly, we obtain by the application of $\underline{\underline{F}} = \underline{\underline{H}}$ in (174) that (165) is invariant for all t.

$$\begin{aligned} H_{nm}(t) &= \sum\sum U_{nK}(t)\, H_{KL}(0)\, U^{-1}_{Lm}(t) \\ &= \sum\sum \delta_{nK} E_K \delta_{KL} \delta^{-1}_{Lm}\, e^{\frac{i}{\hbar}(E_n - E_m)t} \\ &= \sum_L \delta_{nL} E_L \delta^{-1}_{Lm}\, e^{i/\hbar (E_n - E_m)t} \\ &= E_n \delta^{-1}_{nm}\, e^{i/\hbar (E_n - E_m)t} = E_n \delta_{nm}\, e^{i/\hbar (E_n - E_m)t} \\ &= E_n \delta_{nm} \end{aligned}$$

The relation (172) can also be substituted by the differential equation

$$\frac{\hbar}{i}\dot{F}_{n,m} = F_{n,m}(E_n - E_m) \tag{175}$$

or

$$\frac{\hbar}{i}\dot{\underline{F}} = \underline{H}\underline{F} - \underline{F}\underline{H} \tag{176}$$

where by $\underline{H}$ is understood the special diagonal matrix (165). (165) enables the transition from (176) back to the form (172).

The relation (172) signifies nothing else but that in the relation (151) for the calculation of matrix elements we take the functions

$$\psi_n(t) = u_n e^{\frac{i}{\hbar}E_n t} \tag{177}$$

instead of the u_n's, where the $\psi_n'(t)$'s satisfy the wave equation

$$-\frac{\hbar}{i}\dot{\psi}_n = \underline{H}\psi_n$$

Then we have

$$F_{kn} = \int \psi_k^* (\underline{F}\psi_n)\, dq = e^{\frac{i}{\hbar}(E_k - E_n)t} \Big/ u_k^* \underline{E}(u_n)\, dq = e^{\frac{i}{\hbar}(E_k - E_n)t} F_{kn}(0).$$

we can now generalize this state of affairs by introducing an arbitrary orthogonal system φ_n as the basis, without these being necessarily of the special form (177), provided the essential condition is fulfilled that these $\alpha_n(t)$ all satisfy the wave equation

$$-\frac{\hbar}{i}\dot{\varphi}_n = \underline{H}\varphi_n \tag{178}$$

It follows next from the fact that for all solutions of (178) $\int \psi^* \psi\, dV$

is a constant of the time, one has

$$\frac{d}{dt}\int \varphi_n^* \varphi_m \, dV = 0$$

as can be seen by application to the solution $c_n \varphi_n + c_m \varphi_m$ for arbitrary c_n, c_m.

[we cannot straightaway assume $\int \varphi_n^* \varphi_m^* dV = 0$ because the orthogonality has been proved only in case of stationary systems]

Thus the orthogonality and normalisation of the function system ~~are~~ remain unaltered with lapse of time. So then it follows from

$$F_{n,m} = \int \varphi_n^* (\underline{\underline{F}} \varphi_m) \, dq \qquad (180)$$

by differentiation, that for every Hermitian matrix operator $\underline{\underline{F}}$ not containing the time explicitly

$$\frac{\hbar}{i} \dot{F}_{n,m} = \int \left[(\underline{\underline{H}} \varphi_n)^* (\underline{\underline{F}} \varphi_m) - \varphi_n^* (\underline{\underline{F}} \underline{\underline{H}} \varphi_m) \right] dq \quad (\underline{\underline{F}} \text{ does not contain } t)$$

$$= \int \left[\varphi_n^* (\underline{\underline{H}} \underline{\underline{F}} \varphi_m) - \varphi_n^* (\underline{\underline{F}} \underline{\underline{H}} \varphi_m) \right] dq \quad (\because \underline{\underline{H}} \text{ is Hermitian})$$

$$= (\underline{\underline{H}} \underline{\underline{F}} - \underline{\underline{F}} \underline{\underline{H}})_{n,m}$$

[Hermiticity of $\underline{\underline{F}}$ does not appear necessary for this proof, but from general considerations like (153) necessarily $\underline{\underline{F}}$ is Hermitian]

This again leads to the equation

$$\frac{\hbar}{i} \dot{\underline{\underline{F}}} = \underline{\underline{H}} \underline{\underline{F}} - \underline{\underline{F}} \underline{\underline{H}} \qquad (176)$$

but this time without any special assumption about the matrices.

This rule enables the conservation of the V.R for all times when they are satisfied for $t = 0$.

[In the old literature on quantum mechanics one often finds in place of (176) the operator equation

$$\underline{\underline{H}}\,\underline{\underline{t}} - \underline{\underline{t}}\,\underline{\underline{H}} = \frac{\hbar}{i}\,I$$

which arises from (176) formally by putting t for F. It is however not possible to construct a Hermitian operator (for eg. as functions of p and q) which satisfies these equations. It easily follows from this above relation that $\underline{\underline{H}}$ possesses continuously all eigenvalues from $(-\infty$ to $+\infty)$ (vide Dirac) whereas we know that discrete eigen values also can appear for $\underline{\underline{H}}$. We conclude accordingly that it is fundamentally wrong to introduce an operator t, and the time in wave-mechanics is necessarily to be considered as an ordinary number (C-Zahl).]

We now introduce the assumption (which was so far not necessary) that $\underline{\underline{H}}$ also does not contain the time explicitly. Then according to (176) $\underline{\underline{H}}$ is independent of time (Put $\underline{\underline{F}} = \underline{\underline{H}}$). Accordingly there is a time-independent unitary $\underline{\underline{S}}$ which brings $\underline{\underline{H}}$ to the diagonal form

$$\underline{\underline{S}}^{-1}\,\underline{\underline{H}}\,\underline{\underline{S}} = \underline{\underline{E}}$$

This is the same $\underline{\underline{S}}$ which according to

$$\psi_m = \sum_n \varphi_n S_{n,m}$$

brings the ϕ_n to the special form ψ_n given by (177). By transforming back with this $\underline{\underline{S}}$ we then obtain from (173) and (174), when and denoting the diagonal matrix $e^{\frac{i}{\hbar}\underline{\underline{E}}t}\,\delta_{n,m}\,e^{\frac{i}{\hbar}E_n t}$ by $e^{\frac{i}{\hbar}\underline{\underline{E}}t}$, that

$$\underline{\underline{F}}(t) = \underline{\underline{U}}(t)\,\underline{\underline{F}}(0)\,\underline{\underline{U}}^{-1}(t) \qquad (174')$$

with

$$\underline{\underline{U}} = \underline{\underline{S}}\,e^{\frac{i}{\hbar}\underline{\underline{E}}t}\,\underline{\underline{S}}^{-1}$$

[$e^{\frac{i}{\hbar}\underline{\underline{E}}t}$ is the unitary diagonal matrix in the ψ-system, and $S \cdots S^{-1}$ transforms it back to the φ-system]

Here $\underline{\underline{U}}$ is plainly unitary since it arises by multiplication of unitary matrices. Because of

$$\underline{\underline{S}}\,\underline{\underline{E}}\,\underline{\underline{S}}^{-1} = \underline{\underline{H}}$$

one can also write

$$\underline{\underline{U}}(t) \equiv e^{\frac{i}{\hbar}\underline{\underline{H}}t} = \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{i}{\hbar}\underline{\underline{H}}t\right)^n = \lim_{N\to\infty}\left(1+\frac{it}{N\hbar}\underline{\underline{H}}\right)^N \cdots (173')$$

This follows also directly from (176) without reference to the diagonal representation of $\underline{\underline{E}}$.

[Using (174') in (176) we have

$$\frac{\hbar}{i}\dot{\underline{\underline{F}}} = \underline{\underline{H}}\,\underline{\underline{U}}\,\underline{\underline{F}}(0)\,\underline{\underline{U}}^{-1} - \underline{\underline{U}}\,\underline{\underline{F}}(0)\,\underline{\underline{U}}^{-1}\underline{\underline{H}}$$

ie $$\frac{\hbar}{i}\left\{\dot{U}(t)F(0)U^{-1}(t) + U(t)F(0)\,\dot{U}^{-1}(t)\right\} = HUF(0)U^{-1} - UF(0)U^{-1}H$$

ie $$\left(\underline{\underline{H}}\,\underline{\underline{U}} - \frac{\hbar}{i}\dot{\underline{\underline{U}}}\right)\underline{\underline{F}}(0)\underline{\underline{U}}^{-1} - \underline{\underline{U}}\,\underline{\underline{F}}(0)\left(\underline{\underline{U}}^{-1}\underline{\underline{H}} + \frac{\hbar}{i}\dot{\underline{\underline{U}}}^{-1}\right) = 0$$

cf. $\underline{\underline{H}}\,\underline{\underline{U}}$

$$\text{ie } \left(\underline{\underline{H}} - \frac{\hbar}{i}\,\dot{\underline{\underline{U}}}\,\underline{\underline{U}}^{-1}\right)\underline{\underline{F}}(0) - \underline{\underline{F}}(0)\left(\underline{\underline{H}} + \frac{\hbar}{i}\,\underline{\underline{U}}\,\dot{\underline{\underline{U}}}^{-1}\right) = 0$$

$$\text{ie } \left(\underline{\underline{H}} - \frac{\hbar}{i}\,\dot{\underline{\underline{U}}}\,\underline{\underline{U}}^{-1}\right)\underline{\underline{F}}(0) - \underline{\underline{F}}(0)\left(\underline{\underline{H}} - \frac{\hbar}{i}\,\underline{\underline{U}}\,\underline{\underline{U}}^{-2}\dot{\underline{\underline{U}}}\right) = 0.$$

which gives $\underline{\underline{H}} - \frac{\hbar}{i}\,\dot{\underline{\underline{U}}}\,\underline{\underline{U}}^{-1} = 0$ or ~~$\underline{\underline{H}}\,\underline{\underline{U}} - \frac{\hbar}{i}$~~ ie $\underline{\underline{U}} = e^{\frac{i}{\hbar}\underline{\underline{H}}t}$]

We shall prove further that U is similary for the case where all powers of $\underline{\underline{H}}$ exist simultaneously for all f. Firstly

$$\underline{\underline{U}}(t_1)\,\underline{\underline{U}}(t_2) = \underline{\underline{U}}(t_1 + t_2) \qquad (173'')$$

and in particular

$$\underline{\underline{U}}(t)\,\underline{\underline{U}}(-t) = \underline{\underline{U}}(0) = I$$

$$\underline{\underline{U}}^{-1}(t) = \underline{\underline{U}}(-t) = e^{-\frac{i}{\hbar}\underline{\underline{H}}t}$$

and thus for every $U(t)$ there exists a $U(-t)$ for the same function set and thus the existence of the inverse is satisfied. Through successive application of

$$\int g^*(\underline{\underline{H}}^n f)\,dq = \int (\underline{\underline{H}}^n g)^* f\,dq \qquad (\underline{\underline{H}}^n \text{ is Hermitian})$$

for all powers of $(\underline{\underline{H}})^n$ of $\underline{\underline{H}}$ it can be shown that

$$\int g^*(\underline{\underline{U}} f)\,dq = \int (\underline{\underline{U}}^{-1} g)^* f\,dq$$

[$*$Herm like $\frac{i}{\hbar}\underline{\underline{H}}t$ in the expansion of $\underline{\underline{U}}$ gives $\int (\dot{i}\underline{\underline{H}}g)^* = -\int i(\underline{\underline{H}}g)^*$]

and in particular for $g = \underline{\underline{U}} f$

$$\int (\underline{\underline{U}} f)^* (\underline{\underline{U}} f)\,dq = \int f^* f\,dq$$

which leaves the length invariance of U. U satisfies the differential equation

$$\frac{i}{\hbar}\,\dot{\underline{\underline{U}}} = \underline{\underline{H}}\,\underline{\underline{U}}\;; \quad \text{accordingly} \quad \frac{i}{\hbar}\,\dot{\underline{\underline{U}}}^{-1} = -\underline{\underline{U}}^{-1}\underline{\underline{H}} \tag{173'''}$$

which can be verified from (176) by using (174'). Concerning the significance of $\underline{\underline{U}} f$, we remark that $\underline{\underline{U}}$ when applied to the coefficients of the development of f in the fixed system $\varphi_1(0), \varphi_2(0), \ldots$ viz.

$$a_1, a_2, \ldots$$

transforms these into $a_n(t) = \sum_m U_{n,m}\, a_m(0)$. We can however also choose for $a_K(0)$ the special system $\delta(q-q')$. Then $\underline{\underline{U}}$ directly transforms the function $f(0)$ to $f(t)$ so that f satisfies the wave equation and for $t=0$ coincides with the arbitrary function f.

$$f(q,t) = \underline{\underline{U}}(t) f(q,0) = \int U(q,q',t) f(q',0)\, dq' \tag{181}$$

$$U(q,q';0) = \delta(q-q')\;; \quad \frac{\hbar}{i}\frac{\partial}{\partial t} U(q,q',t) = \underline{\underline{H}}\, U(q,q',t) \tag{181'}$$

The length-invariance of $\underline{\underline{U}}$ follows immediately from the continuity equation and is equivalent to

$$\int U(q,q';t)\, U^*(q,q'';t)\, dq = \delta(q'-q'') \tag{182}$$

and further

$$U^*(q',q,t) = U(q,q';-t) = U^{-1}(q,q';t) \tag{182'}$$

and in general

$$\int U(q,q';t_2)\, U(q',q'';t_1)\, dq' = U(q,q'';t_1+t_2) \tag{182''}$$

we recognise these functions U as a generalisation of the equation (60) in § 2

$$U(q,q';t) = U(q-q';t) = e^{-i\pi/4}\sqrt{\frac{m}{2\pi\hbar}}\,\frac{1}{\sqrt{t}}\, e^{\frac{im}{2\hbar}(q-q')^2/t}$$

for the case of a force-free particle moving in one dimension, also of the U-function in (61) for the three-dimensional case built up as a product, and analogously for an arbitrary number of particles. For the case where forces act $\underline{U}$ does not in general depend upon the difference $(q - q')$ of the coordinates and can in general be constructed only through the knowledge of the eigen-solutions $u_n(q)$. Then one has

$$U(q, q'; t) = \sum_n u_n^*(q')\, e^{-\frac{i}{\hbar} E_n t}\, u_n(q) \qquad (183)$$

since then according to (170') the relation (181') is satisfied. The eigen-functions u_n are characterised by

$$\underline{U}\, u_n = e^{-\frac{i}{\hbar} E_n t}\, u_n^* \qquad (184)$$

The existence of an unitary $\underline{U}$ of the kind mentioned must however be assumed as physically necessary. Because this only means that the wave function is solvable for any arbitrary initial function $f(q, 0)$ and can reach at time t every $f(q, t)$. Finally this means shows how any function of time t can be arrived at in course of time with the help of the wave equation.

With this fact is connected the problem of the representation of eigen-values of Hermitian operators which has been exactly formulated in equation (III') §6. First of all we must investigate ~~of~~ steht further the region of definition of the operator $\underline{H}$ on the aggregate of functions f for which $\int |f|^2 dq$ exists. It is not required that $\underline{H} f$ should have a meaning everywhere, since for example it is no longer true for the operator of multiplication say a by a q (thus $\int q^2 |f^2| dq$ does not exist for all f). One can however

desire that the set of functions, for which $\underline{H}f$ has a meaning, lie everywhere dense ie to each f there is a g with a significant $\underline{H}g$ such that besides $\int |f-g|^2 dq$ is arbitrarily small. Further the linear ~~co~~ closure of $\underline{H}$ is to be required ie ~~to~~ from $\lim_{N\to\infty} \int |f-f_N|^2 dq = 0$, and $\lim_{N\to\infty} \int |F-\underline{H}f_N|^2 dq = 0$ should follow $Hf = F$

In the course of penetrating researches on such Hermitian operators J.v. Neumann has shown found the remarkable result that not all such operators admit an eigen value-representation of the form (III'). Furthermore for the possibility for such a representation requires the transformability of $\underline{H}$ to an unitary operator $\underline{U}$, and this is the necessary and sufficient condition for the existence of the eigenvalue spectrum. An unitary operator admits accordingly without exception an eigenvalue representation, which has the form

$$(\underline{U}f) = \int_0^{2\pi} e^{iE}\, d(\underline{P}_E f) \qquad (185)$$

analogous to (III'). Here $\underline{P}_E$ and $\underline{P}_{E-E'}$ are the projection operators with the properties (I), (II). The eigen value of an unitary operator has besides ~~was~~ always the ~~value 1 to~~ modulus 1. For unitary operators with the property (176) the eigen-value representation can even be written simultaneously for all t in the form

$$\underline{U}(t)f = \int_{-\infty}^{+\infty} e^{-i\frac{E}{\hbar}t}\, d(\underline{P}_E f) \qquad (185')$$

With the idea of transforming $\underline{H}$ to a unitary $\underline{U}$ Neumann considers the special

operator

$$\underline{\underline{U}} = \frac{1 + i\,\underline{\underline{H}}}{1 - i\,\underline{\underline{H}}}$$

wherefrom it can be shown that $\underline{\underline{U}}$ has everywhere a meaning. This special choice of $\underline{\underline{U}}$ does not however appear essential, thus for eg the operator

$$\underline{\underline{U}}(t) = \lim_{N \to \infty} \left(1 + \frac{it}{kN}\,\underline{\underline{H}}\right)^N$$

can serves the same purpose, and seems to be nearer to physical interpretation.

It might now be mentioned that there has been shown to be an exceptional operator $\underline{\underline{H}}$ which essentially does not allow an unitary continuation in this manner. We shall show here briefly that it is in no way "pathological" but can be simply interpreted physically. We consider a particle which is moving along the x-axis (one-dimensional problem) but at $x = 0$ it is reflected by a perfectly elastic wall so that it is constrained to move only in the half-space $x > 0$. i.e. we consider as allowable certain functions f, which are defined for $0 < x < \infty$ for which $\int_{-\infty}^{+\infty} |f|^2 dx$ exists and which vanishes besides for $x = 0$ or $f(0) = 0$. In this function space $v\,\underline{\underline{p}}_x = v\,\frac{\hbar}{i}\,\frac{\partial}{\partial x}$ is an admissible Hermitian operator (v is a constant of the dimension of velocity, so that $v\,\underline{\underline{p}}_x$ has the dimensions of an energy); firstly its region of application is everywhere dense, secondly on account of $f(0) = 0$ it satisfies the Hermiticity condition viz

$$\int_0^\infty g^* \left(\underline{\underline{p}}_x f\right) dx - \int_0^\infty \left(\underline{\underline{p}}_x g\right)^* f\, dx = \left[f g^*\right]_0^\infty = 0$$

For this operator there exists however no eigenvalue representation

in the space considered! This becomes clear, when we consider the solutions of the equation

$$-\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = v\underline{p}_x\psi = \frac{\hbar}{i}v\frac{\partial\psi}{\partial x} \quad \text{or} \quad \frac{\partial\psi}{\partial t} = -v\frac{\partial\psi}{\partial x}.$$

These are of the form

$$\psi(x,t) = f(x-vt) \tag{186}$$

Moreover there is a solution in the time-interval $0 < t < \tau$ when and only when for all t of this interval $f = 0$ for $x = 0$. Accordingly $f(\xi)$ must be defined for $-v\tau \leqq \xi < \infty$, and besides

$$f(\xi) = 0 \quad \text{for} \quad -v\tau \leqq \xi \leqq 0 \tag{186'}$$

i.e. $\psi(x,\tau) = 0$ for $0 \leqq x \leqq v\tau$; $\psi(x,\tau) = f(x-v\tau)$ for $v\tau \leqq x < \infty$ (186")

In fact only when (186") is satisfied, on account of (186)

$$\int_0^\infty |\psi(x,\tau)|^2 dx = \int_0^\infty |\psi(x,0)|^2 dx$$

The representation $\underline{U}$ which transforms $f(x)$ into the $\psi(x,\tau)$ defined in (186") is surely certainly length-invariant, but not unitary. Because the aggregate of $\psi(x,\tau)$ is less than the aggregate of $f(x)$ or what is the same thing the operator $\underline{U}^{-1}$ inverse to $\underline{U}$ does not exist for all $f(x)$, but only for such $f(x)$ as vanish in the interval $0 \leqq x \leqq v\tau$; for the remaining f there exists no solution of the wave equation in the interval $-\infty < \tau < t < 0$. Should that the first N powers of $\underline{p}_x$ should have simultaneously a meaning in the space considered, the original function f must be N-fold differentiable, where as high a power N is required. Such

an operator cannot surely be allowed as a Hamilton function. On the contrary the operator $\partial^2/\partial x^2$ shows a normal behaviour in the space considered, and has the eigen-functions $\sin Kx$; equally natural is the operator $\frac{\hbar}{i}\frac{\partial}{\partial x}$ in ordinary space $-\infty < x < +\infty$. Exactly like the operator $\frac{\hbar}{i}\frac{\partial}{\partial x}$ in half space behaves the radial momentum operator $\underline{p}_r f = \frac{\hbar}{i r}\frac{\partial}{\partial r}(rf)$ in ordinary space. It is hermitian but its matrices cannot be brought to the diagonal form. This is however possible for the operator $\underline{p}_r^2 f = -\hbar^2 \frac{1}{r}\frac{\partial^2}{\partial r^2}(rf)$ appearing in the Hamiltonian function, and the operator has the eigen functions $\sin Kr/r$.

§ 9. Determination of the stationary states of a system by measurement. General discussion of the concept of measurement.

Before we proceed to the general discussion of the behaviour of a system under the action of external perturbations, we shall take on hand certain typical examples to decide the method in which the measurement of a stationary state by external agency is carried out. Here it is essential to observe that a system, even when it is closed from outside, must not necessarily find itself in a stationary state, what is the same thing, must not possess any sharp particular value of its energy with certainty. The most general state of a system is moreover most often given by

$$\psi = \sum_n c_n(0)\, e^{-\frac{i}{\hbar}E_n t} u_n(q) = \sum c_n(t)\, u_n(q) \qquad (187)$$

with time-independent, but nevertheless arbitrary coefficients $c_n(0)$. (In case a continuous spectrum appears the summation is to be replaced by an integral). In the general case a stationary state of the system is produced by the measuring apparatus. We have now to investigate how the transition is to be represented with the aid of the mathematical formalism of wave mechanics. Thereby follows as a principal result a simple statistical meaning for the coefficients c_n.

The simplest way of investigating the states of a system (atoms or molecules) consists in bringing in an external field which reacts in different ways on the system in different states. Let Q signify the coordinates of the centre of gravity of the molecules or atoms; we can first write an arbitrary function $\psi(q, Q; t)$ in the form

$$\psi(q, Q; t) = \sum c_n(Q, t)\, u_n(q, Q).$$

Here q signifies the coordinates of the particles of the system relative to their centre of gravity, $u_n(q, Q)$ the eigenfunction with the eigenvalue $E_n(Q)$ which belongs to the corresponding functions $\Phi_k(q, Q)$ and $V(q, Q)$ of the external potential, and the eigenfunction satisfying the equation analogous to (97)

$$-\sum_{a=1}^{N} \frac{\hbar^2}{2m^{(a)}} \sum_{k=1}^{3} \left[\left(\frac{\partial}{\partial x_k^{(a)}} - \frac{ie^{(a)}}{\hbar c} \Phi_k\left(x^{(a)} + Q\right) \right)^2 + V^{(a)}\left(x^{(a)} + Q\right) + V(q_1 \cdots q_f) \right] u_n(q, Q)$$

$$= E_n(Q)\, u_n.$$

In this Q officiates as an external parameter. When the external field only varies slightly inside the region of extension of the system, $\Phi_k(x^{(a)} + Q)$ and $V^{(a)}(x^{(a)} + Q)$ can be developed in a series which, usually, can be broken off after

a small number of terms, or most often even after the first term.

$$\Phi_k\left(x^{(a)}+Q\right) = \Phi_k(Q) + \sum_{l=1}^{3} \frac{\partial \Phi_k}{\partial Q_l} x_l^{(a)} + \dots$$

$$V^{(a)}\left(x^{(a)}+Q\right) = V^{(a)}(Q) + \sum_{l=1}^{3} \frac{\partial V^{(a)}}{\partial R_l} x_l^{(a)} + \dots$$

From the complete equation wave equation for Ψ we obtain, apart from the additional terms omitted here, the wave equation for the $C_n(Q,t)$ in the form

$$-\frac{\hbar}{i}\frac{\partial C_n}{\partial t} = -\frac{\hbar^2}{2M}\sum_{l=1}^{3}\frac{\partial^2 C_n}{\partial Q_l^2} + E_n(Q)\,C_n \qquad (188)$$

The physical significance of this wave equation is that the eigen-values of the inner energy which depends upon the position of the centre of gravity of the system appears simply as the potential energy for the motion of the centre of gravity of the whole system.

As regards the nature of the omitted additional terms we shall discuss them in detail in § 11; we notice here that they hinder the separability of the wave equation in the C_n's because all C_n's and their first derivatives appear in them etc. Its action is small, in case the motion of the system is so slow that during the time $\tau = \hbar/(E_n - E_m)$ the mean change in position $\Delta Q = \bar{Q}(t+\tau) - \bar{Q}(t)$ of the system satisfies the condition

$$\frac{\partial E_n}{\partial Q}\Delta Q \ll (E_n - E_m) \qquad (189)$$

A special precaution is in place, for those cases where the concerned state of the system is distorted in the absence of external force fields so that certain energy-

differences $(E_n - E_m)$ are proportional to the intensities of external fields. Also in such cases the inequality (189) is the condition for the applicability of the wave equation (188).

Wave equations of this type form the basis of all experiments which are concerned with the deflection of molecular rays in external force fields. In case there is no distortion is present due to appears due to the presence of an external field, one can consider a different excitation state which belongs to a zero total angular momentum and is split by an external electric field. If F is the electric field strength at the position Q, we can assume in general for $E_n(Q)$ the form

$$E_n(Q) = -\frac{\alpha_n}{2} F^2(Q) \qquad (190)$$

where $\alpha_n, \ldots \alpha_m, \ldots$ denote the values of the electrical polarisabilities of the atoms or molecules in the states $n, m, \ldots$

In the original form of the experiments conducted by Stern and Gerlach on molecular rays, where only directions with different moments of momentum were separated and not those systemstates with different excitation states of the atoms, the energy of the considered state was is given by

$$E_m = E_0 + h\,o\,m \qquad (191)$$

where m is the magnetic quantum number running from $-j$ to $+j$ (half or completely integral) and the magnitude o proportional to the external magnetic field strength H is the Larmor frequency multiplied by the Landé factor g

$$0 = g \cdot \frac{eH}{2m_0 c} \qquad (192)$$

The condition (189) here states that the values of the components of H along three fixed space directions at the place of the atom may only vary relatively little in the course of the time $1/\sigma$.

We can now discuss on the basis of the wave equation (188) ~~which~~ the circumstances under which the rays ~~can be separated~~ which belong to states n and m can be separated spatially through the external field. Let us imagine a cylindrical bundle of rays of cross-section d running along the x-direction. According to (82) the centre of gravity of the wave packet moves along a classical orbit belonging to a potential function $E_n(Q)$, and according to (84), (85) and the uncertainty relation the extension of the wave-packet varies corresponding to the necessary presence of an initial momentum of at least $p_y \sim \frac{h}{d}$ in the cross-direction to the ray. This can also be thought of as due to a diffraction of the ray in passing through a limited aperture of dimension d. We have now to calculate on one hand the deflections $y_n, \cdots y_m, \cdots$ of the rays corresponding to states $n, \cdots m, \cdots$ in the y-direction in time t due to the force-field. On the other hand the broadening Δy of the rays in the cross-direction due to the well-known diffraction effect is to be calculated at the same time t. To obtain two clearly separated rays

$$y_n - y_m \gg \Delta y \qquad (193)$$

Now, $y_n = \frac{1}{2m} \frac{\partial E_n}{\partial a} t^2$; $y_m = \frac{1}{2m} \frac{\partial E_m}{\partial a} t^2$

$$\Delta y \sim \frac{\hbar}{Md} t$$

accordingly the condition (194) gives

$$\frac{\partial (E_n - E_m)}{\partial Q_y} t \gg \frac{\hbar}{d} ; \quad d \frac{\partial (E_n - E_m)}{\partial Q_y} \gg \hbar \tag{194}$$

The frequency ν_{nm} belonging to the energy-difference $(E_n - E_m)$ amounts to

$$\nu_{nm} = \frac{E_n - E_m}{\hbar} \tag{195}$$

Denoting by $\delta f = d \frac{\partial f}{\partial Q_y}$ the variation along the cross-dimension of a ray,

$$t \delta \nu_{n,m} \gg 1 \tag{194'}$$

In every case we have further $\delta \nu_{nm} < \nu_{nm}$ (actually $\delta \nu_{nm}$ would be even essentially less than ν_{nm}) so that also

$$t \nu_{nm} \gg 1 \tag{196}$$

The determination as to whether the system is in state m or state n cannot be made in an arbitrarily short time, but necessitates a minimum time

$$t \sim \frac{1}{\nu_{n,m}} = \frac{\hbar}{E_n - E_m} \tag{196'}$$

In the case of the original Stern-Gerlach experiments where the energy-value is given by (191), this time amounts to $1/0$. We will see that this minimum time is valid for all methods of determination and not merely for the case here considered.

The characteristic of the deflexion experiments lies in this that

that after carrying them out the molecule or atom ⊗ practically certainly (obviously depending on time) lies in completely separated regions V_n, V_m ... in case the molecule was initially certainly in states n, m, .. When initially $c_n = 1$, $c_m = 0$ for $n \neq m$, the solution would be through the transition

$$\psi_n(q, Q; t) = a_n(Q, t)\, u_n(q, Q) \tag{197}$$

Here $u_n(q, Q)$ is orthogonal with respect to q for a fixed Q, and besides the dependence of u on Q falls out if the atom moves in a region of space where the external force is constant. As a consequence of the continuity equation, we have further

$$\int a_n^* a_n \, dQ = 1; \quad \int a_n^* a_m \, dQ = 0 \text{ for } n \neq m \tag{198}$$

and on account of the postulated property of the deflexion experiments

$$a_n(Q, t) = 0 \quad \text{outside } V_n(t) \tag{199}$$

The linearity of the wave equation which is necessarily used here further shows that for the case where we have to do with initially with the general inner state $\sum_{(n)} c_n u_n(q)$, the wave function after the deflexion experiment takes the form

$$\psi(q, Q; t) = \sum c_n \psi_n(q, Q; t) = \sum c_n a_n(Q, t)\, u_n(q, Q) \tag{200}$$

The probability, that ~~as to which~~ whatever value q has ~~simultaneously when~~ of the position Q ~~lies~~ in the region $(Q, Q + dQ)$ is given according to the

general principles already developed by

$$W(Q)\,dQ = dQ \int \psi^* \psi(q, Q; t)\,dq = \sum_{(n)} |c_n|^2 |a_n(Q,t)|^2\,dQ \qquad (201)$$

According to (199) we find further that the probability in order that the atom is in general found in the region V_n is given by

$$\int_{V_n} W(Q)\,dQ = |c_n|^2 \qquad (202)$$

This can by definition asserted as equivalent to the following: In the general case $|c_n|^2$ is the probability in order that the system be found in state E_n.

The justification for such a determination follows from the result for the probability that, after the deflexion experiment, q is found in $(q, q+dq)$ whatever be the value Q. We find according to (200) and (198)

$$W(q)\,dq = dq \int \psi^* \psi(q, Q; t)\,dQ = \sum_{(n)} |c_n|^2 |u_n|^2 dq \qquad (203)$$

Here it is assumed that the u_n are no longer any more dependent on Q as was the case in the above discussion. An exactly similar result follows for the probability $W(p)\,dp$ in momentum space.

We can consider for the atom centre of gravity as special measuring apparatus (whereby it is only necessary that one should add a new degree of freedom to the system), the energy E_n of the inner state being the quantity to be measured. In place of the centre of gravity certain other apparatus might

be taken ( ) which is indeterminate

in only so far as that the apparatus certainly reacts differently on different states E_n, as is expressed in equation (199). The consequential absence of the degree of freedom of the apparatus, which can be determinately estimated by formally by integration of the probability over q has according to (203) the consequence that the phases of the amplitudes c_n which correspond to the measured quantities, no longer appear in the result. The probability that a certain magnitude ξ characterising the system should be found between ξ, $\xi + d\xi$ is then the equal to the sum of the probabilities for the cases, where the measured quantities have determinate values, multiplied by chosen weight factors $|c_n|^2$

$$W(\xi)\, d\xi = \sum_n |c_n|^2 W_n(\xi)\, d\xi \quad \left(\sum_n |c_n|^2 = 1\right); \tag{203'}$$

in particular is this true for the conjugate magnitudes q and p, where $W_n(q) = |u_n(q)|^2$; $W_n(p) = |v_n(p)|^2$. In this case we consider call the considered totality a mixture. In contrast to this we have the pure case for which the probability $W(\xi)$ cannot be generated simultaneously for all magnitudes ξ (or what is more satisfactory, for two conjugate magnitudes ξ) by the addition of the probabilities for all the possible cases. The carrying out of the measurement of the inner energy E_n of the system including of the

of the consequential abstraction of the degree of freedom of the apparatus produces accordingly a pure case for which

$$W(q)\,dq = \left|\sum c_n u_n(q)\right|^2 dq\,; \quad W(p) = \left|\sum c_n v_n(p)\right|^2 dp\,, \text{ and}$$

in general (ie when it does not happen that all c_n's except one vanish) a mixture for which

$$W(q)\,dq = \sum_n |c_n|^2 |u_n(q)|^2 dq\,; \quad W(p)\,dp = \sum_n |c_n|^2 |v_n(p)|^2 dp.$$

This result which follows from the assumptions so far made and not any new ones, and as a necessary consequence of the linearity of the wave equation is of decisive importance for [illegible] the picturing (without contradiction) of the concept of measurement in wave mechanics. This is because it shows that one is led to the satisfactory result that one can draw the line between the system observed and described by the wave function, and the measuring apparatus.

The situation that a determinate measuring apparatus can be used can therefore be described directly in terms of the mathematical formalism of wave-mechanics. It is however, on the contrary, otherwise with the determination (statement) that the measurement gives a completely determinate result; in our case with such statements as "the atom has accordingly the value E_n and no other"; "the centre of gravity of the atom is in the region V_n after the experiment". Such a fixing of a physical fact by the help of a measurement not connected with the system cannot be brought into the framework of the mathematical formalism which only deals with possibilities (or probabilities). This is entirely on a par with the measurement of position of a

of a particle. In this case instead of $\sum c_n u(q)$ we have the function $\psi(q,t)$ and instead of Q we have the position of the light-quantum in the focal plane of the eyepiece of the γ-ray-microscope. As mentioned earlier in §1 the necessity for such a special act of observation is not surprising when we observe that every measurement brings about in many cases an uncontrollable interaction in principle between the system and the measuring apparatus. It is here necessary to remark that while the old quantum theory spoke of the "transition processes" between the different stationary states of the system we now have a method of expression free from contradictions according to which the system necessarily possesses a determinate inner energy or finds itself in a stationary state without making use of the fixing of the system by measurement.

What applies to the measurement of energy can be usually applied in quantum mechanics equally to any "arbitrary physical quantity" we shall speak of this generalisation later, because as we have seen measurements of such physical quantities require, in general, a minimum time and it requires a special investigation to find the variation of the quantity in course of time (See § 10). For the measurement of the energy no such complication arises because it is a time constant. In fact the probability that the energy of the system amounts to E_n is given by $|c_n|^2$ and since $c_n(t) = c_n(0)\, e^{-\frac{i}{\hbar} E_n t}$, we have

$$|c_n(t)|^2 = |c_n(0)|^2 \qquad (204)$$

The probability that a certain value E_n is found for the energy of a closed system

is independent of the time. This is the most general form of the energy-theorem. The previously proved theorem that the expectation value $\bar{E}$ of the energy is a time-constant is contained here as a special case since this the expectation value is given by.

$$\bar{E} = \sum_n |c_n|^2 E_n \qquad (205)$$

It is useful to introduce here the density-matrix $\underline{P}$ defined by von J. v. Neumann which in a useful way serves to determine the expectation values of certain magnitudes for a state.

If we have a state which corresponds to the Eigenfunction

$$\psi = \sum_n c_n(0)\, \psi_n(q,t) = \sum_n c_n(0)\, e^{-\frac{i}{\hbar} E_n t}\, u_n(q)$$

we define, in the representation of matrices, for which $\underline{H} = \underline{E}$ is a diagonal matrix.

$$P_{m,n} = c_n^*(t)\, c_m(t) \qquad (206)$$

The mean-value of the energy is given by.

$$\bar{E} = \sum_n P_{nn} E_n = \sum_n (PE)_{n,n}$$

$$\left[\bar{E} = \int \left[\sum_n c_n^* u_n^* \underline{\underline{E}} \cdot \sum_m c_m u_m \right] dq = \int \left[\sum c_n^* u_n^* \sum_{m,n} c_m \delta_{nm} E_n \right] dq \right.$$

$$\left. = \int \left[\sum_n \left(c_n^* u_n^* u_n E_n c_n \right) \right] dq = \sum_n c_n^* c_n E_n = \sum P_{nn} E_n \right].$$

The mean value of q is

$$\bar{q} = \int q \psi^* \psi \, dq = \sum_{n,m} c_n^* c_m \int q \, \psi_n^* \psi_m \, dq = \sum_{n,m} c_n^* c_m q_{n,m}$$

$$\text{or} \quad \bar{q} = \sum_{n,m} q_{nm} P_{m,n} = \sum_n \left(\underline{\underline{q}}\, \underline{\underline{P}} \right)_{n,n}$$

Also the mean value of an arbitrary operator $\underline{\underline{F}}$ is given by

$$\bar{F} = \int \psi^* (\underline{\underline{F}} \psi)\, dq = \sum_{n,m} c_n^*(t)\, c_m(t)\, F_{n,m}(0) = \sum_{n,m} F_{n,m}(0)\, P_{m,n} = \sum_n (\underline{\underline{F}}\,\underline{\underline{P}})_{n,n}$$

Now the <u>spur</u> of a matrix X is defined as the sum of its diagonal elements

$$\text{Spur}\,(\underline{\underline{X}}) = \sum_n X_{n,n} \qquad (207)$$

This Spur has the important property that the Spur of the product of two matrices A and B is commutative ie independent of the order of the factors

$$\text{Spur}\,(\underline{\underline{A}}\,\underline{\underline{B}}) = \text{Spur}\,(\underline{\underline{B}}\,\underline{\underline{A}}) \qquad (208)$$

[This is because $\text{Spur}\,(\underline{\underline{A}}\,\underline{\underline{B}}) = \sum_n (\underline{\underline{A}}\,\underline{\underline{B}})_{n,n} = \sum_n \sum_m A_{n,m} B_{m,n}$

and $\text{Spur}\,(\underline{\underline{B}}\,\underline{\underline{A}}) = \sum_m (\underline{\underline{B}}\,\underline{\underline{A}})_{m,m} = \sum_m \sum_n B_{m,n} A_{n,m}$]

If, in (208), we put $A = S^{-1}X$; $B = S$ we obtain the following important relation

$$\text{Spur}\,(\underline{\underline{S}}^{-1}\,\underline{\underline{X}}\,\underline{\underline{S}}) = \text{Spur}\,(\underline{\underline{X}}) \qquad (209)$$

<u>In particular the Spur of a matrix is invariant for unitary transformations of the matrix.</u>

our earlier result concerning the mean value of an operator F for the most general state of the system can be expressed with the aid of the density matrix $\underline{\underline{P}}$ as

$$\bar{F} = \text{Spur}\,(\underline{\underline{P}}\,\underline{\underline{F}}) = \text{Spur}\,(\underline{\underline{F}}\,\underline{\underline{P}}) \qquad (210)$$

In particular it is allowed to substitute for $\underline{F}$ a position coordinate q, or a momentum coordinate p or the energy $\underline{H}$ of the system.

This expression is however, on account of (209), invariant for a change in the representation of the matrices. For eg. when q is brought to the diagonal form

$$\bar{F} = \int P(q', q'')\, F(q', q'')\, dq'\, dq''$$

accordingly for eg. with

$$P(q', q'') = \psi(q', t)\, \psi^*(q'', t); \quad F(q'q'') = F(q')\, \delta(q'' - q')$$

$$\bar{F}(q) = \int \psi^*(q, t)\, F(q)\, \psi(q, t)\, dq$$

as it must be. Further the dependence of $\underline{P}$ on time is so chosen that by the independence of $\underline{F}$ on time, the mean value of F has the right dependence on time. In fact one has, according to (206)

$$\frac{\hbar}{i}\, \dot{P}_{m,n} = P_{mn}\, E_n - E_m\, P_{m,n},$$

and accordingly, in general,

$$\frac{\hbar}{i}\, \dot{\underline{P}} = -(\underline{H}\,\underline{P} - \underline{P}\,\underline{H}) \qquad (211)$$

and this when substituted in ~~(200)~~ (210) gives correctly (in consonance with (176))

$$\dot{\bar{F}} = \text{Spur}(\dot{P}F) = -\text{Spur}(HPF) + \text{Spur}(PHF)$$

$$= -\text{Spur}(PFH) + \text{Spur}(PHF)$$

$$= -\text{Spur}(P, FH - HF) = \overline{HF - FH}$$

one also notices that the sign in (211) is the reverse of that in (176).

So far we have only considered the pure case. As follows from (206) in the most general (pure) case the matrix $\underline{\underline{P}}$ can be brought to the diagonal form unitarily, and is readily seen to be equal to $P_{n,m} = \delta_{n,m}$; accordingly $\underline{\underline{P}} = \begin{pmatrix} 0 & & & \\ & 0 & & \\ & & 1 & \\ & & & 0 \\ & & & & 0 \end{pmatrix}$. One of the eigen-values of $\underline{\underline{P}}$ is accordingly 1, the rest are zero. We will see that this is also a sufficient condition for a pure case.

As v. Neumann has remarked, we can now so generalise the matrix $\underline{\underline{P}}$ that the relations (210) and (211) also hold for the mixture. The matrix $\underline{\underline{P}}$ of the most general mixture arises by a linear combination of possible matrices $\underline{\underline{P}}_1, \underline{\underline{P}}_2, \cdots$ of the pure cases according to

$$\underline{\underline{P}} = \sum p_n \underline{\underline{P}}_n \tag{212}$$

where $$\sum_{(n)} p_n = 1; \qquad p_n \geq 0 \tag{212'}$$

We see that on account of $\mathrm{Spur}(\underline{\underline{P}}_n) = 1$ for all $\underline{\underline{P}}_n$ according to (212') it follows in general

$$\mathrm{Spur}(\underline{\underline{P}}) = 1 \tag{213}$$

This relation is in fact necessary because of (210), as we can easily recognise, by substituting for $\underline{\underline{F}}$ the unit matrix. We state that $\underline{\underline{P}}$ is positive definite ie that all the eigen-values of $\underline{\underline{P}}$ which do not vanish are

positive.

Negative eigen. values of P do not exist (214)

This assertion is equivalent to the other that for all (Hermitian) operators, which are quadratic, one has

$$\text{Spur}\,(\underline{P}\,\underline{A}^2) \geqq 0 \qquad (\underline{A} \text{ Hermitian}) \tag{214'}$$

If $\underline{P}$ be brought to the diagonal form it follows from (214')

$$\sum_n P_{n,n} \sum_k |A_{nk}|^2 \geqq 0$$

for all $A_{n,k}$, accordingly $P_{nn} > 0$ for all n. It follows conversely that (214') is valid for this special representation of matrices on account of the general invariance of the Spur. From (214') it can now be perceived: the sum of two positive definite matrices is again positive definite. Besides the sum of several positive matrices can vanish only when all the matrices separately vanish. Since $p_n\,\underline{P}_n$ are positive definite matrices we recognise now that (214) is in fact a consequence of (212). Conversely the most general Hermitian matrix which satisfies the conditions (213) and (214) can be brought to the form (212) such that the matrices $\underline{P}_n$ refer to the pure case, and can even be assumed to be commutative. For example let us imagine $\underline{P}$ brought to the diagonal form P_{nn}; one need only put $p_n = P_{nn}$, while $\underline{P}_n$ has the element 1 only at the place n but everywhere else zero.

[P. T. O

Argument to prove (214)

(i) $p_n \underline{P}_n$ are $+^{ve}$ definite ($p_n \geq 0$)

(ii) Sum of 2 $+^{ve}$ def. matrices is $+^{ve}$ definite (This follows

(iii) Hence (214).

We can now characterise simply the pure case along with the general matrices ρ which satisfy only the conditions (213) and (214) by the relation

$$\underline{\underline{\rho}}^2 = \underline{\underline{\rho}} \qquad (215)$$

A Hermitean matrix satisfies this relation when and only when all its eigen-values satisfy it ie when these eigen-values are $-1, 0$ or $+1$. The possibility of the eigen-value -1 is excluded because of (214) and from (213) it then follows that only one of the eigen-values is 1 and the rest are zero. In the general case $\rho - \rho^2$ is always a positive matrix, since the eigen values of ρ are always less than 1 on account of (213).

We shall also show further that by bringing together two totalities to which belong the density matrices Q and R according to

$$\underline{\underline{\rho}} = p_1 \underline{\underline{Q}} + p_2 \underline{\underline{R}} \quad (0 < p_1 < 1,\ 0 < p_2 < 1,\ p_1 + p_2 = 1)$$

a new pure case can never again come up, and if so then $\underline{\underline{Q}} = \underline{\underline{R}} = \underline{\underline{\rho}}$.

To prove this let us form

$$\underline{\underline{\rho}}^2 = p_1^2 \underline{\underline{Q}}^2 + p_1 p_2 (\underline{\underline{Q}}\,\underline{\underline{R}} + \underline{\underline{R}}\,\underline{\underline{Q}}) + p_2^2 \underline{\underline{R}}^2$$

one has $$(\underline{\underline{Q}} - \underline{\underline{R}})^2 = \underline{\underline{Q}}^2 - (\underline{\underline{Q}}\,\underline{\underline{R}} + \underline{\underline{R}}\,\underline{\underline{Q}}) + \underline{\underline{R}}^2$$

and hence, $$\underline{\underline{\rho}}^2 = p_1 \underline{\underline{Q}}^2 + p_2 \underline{\underline{R}}^2 - p_1 p_2 (\underline{\underline{Q}} - \underline{\underline{R}})^2$$

(in view of $p_1 + p_2 = 1$, $p_1^2 + p_1 p_2 = p_1$; $p_2^2 + p_1 p_2 = p_2$). Thus we find

$$\underline{\underline{\rho}} - \underline{\underline{\rho}}^2 = p_1 (\underline{\underline{Q}} - \underline{\underline{Q}}^2) + p_2 (\underline{\underline{R}} - \underline{\underline{R}}^2) + p_1 p_2 (\underline{\underline{Q}} - \underline{\underline{R}})^2$$

on the right hand side of which appear only positive matrices. If $\underline{\underline{P}}$ belongs to a pure case, then on account of $\underline{\underline{P}}^2 = \underline{\underline{P}}$ all the matrices on the right hand side vanish separately, in particular

$$(\underline{\underline{Q}} - \underline{\underline{R}})^2 = 0$$

The square of a Hermitian matrix can only vanish when all the elements of the matrix themselves vanish [we can see this from $(A^2)_{n,n} = \sum_K |A_{nK}|^2$].

Accordingly

$$\underline{\underline{Q}} = \underline{\underline{R}} \qquad \text{Q.E.D.}$$

The definition of a pure case as a certain totality for which one eigenvalue of the density matrix is 1, the rest being zero is also equivalent to the other definition that a pure case cannot be produced by mixing up two different totalities.

V. Neumann has shown further that the quantity

$$\Sigma \equiv \text{Spur}\,(\underline{\underline{P}} \log \underline{\underline{P}}) \qquad (216)$$

except for the factor $1/R$ (R = Boltzmann's constant) plays the role of entropy for the density distribution P. For the pure case, and only in that case does it vanish, since $P_{nn} \log P_{nn} = 0$ is valid for $P_{nn} = 0$ as also for $P_{nn} = 1$. Assuming that (213) and (214) always hold, we have accordingly

$$\text{Spur}\,(\underline{\underline{P}} \log \underline{\underline{P}}) = 0 \qquad (215')$$

a condition equivalent to (215). A certain distribution $\underline{\underline{P}}$ which for a given mean value

$$\bar{E} = \text{Spur}\,(\underline{\underline{H}}\,\underline{\underline{P}})$$

of the energy makes the quantity Σ a minimum is the canonical distribution

$$\underline{\underline{P}} = Ce^{-\underline{\underline{H}}/\Theta} \tag{217}$$

where Θ is a constant which has the significance of k times the temperature, and while C is determined from the normalisation condition (213). The free energy is then given by

$$e^{-F/\Theta} = Spur\left(e^{-\underline{\underline{H}}/\Theta}\right) \tag{218}$$

so that (217) can also be written as

$$\underline{\underline{P}} = e^{(F-\underline{\underline{H}})/\Theta} \tag{217'}$$

If $\underline{\underline{H}}$ be brought to the diagonal form, so also is P diagonal, and

$P_{n,n} = e^{-E_n/\Theta}$, and according to (218)

$$e^{-F/\Theta} = \sum_n e^{-E_n/\Theta} \tag{218'}$$

The method of measurement of the energy of the system so far described has the property that an immediate repitition of the measurement gives the same value for the measured quantity as the first measurement. Or in other words: In the case where the result of the application of the measuring apparatus is not given as known, but only the fact of this application (in the terminology of §1 the measured quantity is unknown after the measurement but determinate), the probability that the measured quantity has a certain value is the same before and after the measurement. We shall denote such measurements as of the first kind.

On the other hand it might also happen that the system may vary in an uncontrollable manner by the measurement — even such that before the measurement

the quantity to be measured has with certainty a determinate value. The result of repeated measurement on this method is then not the same as that of the first measurement. It is therefore even possible to make a previous conclusion about the result of the measurement of the magnitude of the concerned system even before the measurement. We call such a measurement one of the second kind. We have already seen in § 2 that measurement of momentum of the first kind is possible only in long intervals of time, the measurement of momentum of the second kind being however possible in short intervals.

An example for measurement of energy of the second kind is the influence on an atomic system by collisions, where the energy of the colliding particles is measured after the collision. Let at time $t = 0$ the measured system be in state n, and the colliding particle the initial Kinetic energy ϵ. The probability that at time t, the system is in state m, and the colliding particle possesses a Kinetic energy ϵ' lying between ϵ' and $\epsilon' + d\epsilon'$ is given by an expression of the form

$$W_{nm}(\epsilon')\,d\epsilon' = A_{n,m} \left| \frac{1 - \cos\left(E_n + \epsilon - E_m - \epsilon'\right) t/\hbar}{E_n + \epsilon - E_m - \epsilon'} \right|^2 d\epsilon' \qquad (219)$$

(This formula follows from the general formalism of perturbation theory. See § 10, eqn (241,)). In the above we might consider the expression as having been obtained after integration over the initial and final momenta, and the energy being connected with the momentum according to the relation

$\epsilon = p^2/2m$; $\epsilon' = p'^2/2m$ The bracket expression is sensibly different from zero at time t, if

$$E_m - E_n - (\epsilon - \epsilon') \sim \hbar/t$$

for the case $t \gg \hbar/|E_m - E_n|$, as in (196'). Accordingly the measured value of $\epsilon - \epsilon'$ lies in the neighbourhood of the difference $E_l - E_n$ (for some l) when the system is in state n, and in the neighbourhood of $E_l - E_m$ when in state m. Under the known condition for the time, the interval of $\epsilon - \epsilon'$ in which $W(\epsilon')$ is sensibly different from zero is thus significantly separated out. In this manner it can be decided as to whether the original system possesses the energy E_n or E_m.

This experiment would be perhaps simpler if the system is ionized by the collision, so that the energy E_m would be continuous and instead of (219) we can write

$$W(\epsilon', E)\, d\epsilon' dE = A_n(E') \left[\frac{1 - \cos\left((E_n + \epsilon - E' - \epsilon')\, t/\hbar\right)}{E_n + \epsilon - E' - \epsilon'} \right]^2 d\epsilon' dE' \qquad (219')$$

Then the measurement of ϵ, ϵ' and E' is possible by well known methods, and one finds $E' + \epsilon' - \epsilon$ surely in the neighbourhood of E_n, except for variation by $\hbar/t$, if n be the state of the system before collision.

For this consideration the validity of the conservation of energy for collision processes is essential. Besides it has been shown, that inside the region of the inequality (196') the interaction energy of the system is negligible for the energy balance. In this manner it is again justified

to consider E_n as the energy value of the system.

We now proceed to investigate what conclusions can be drawn from the collision experiments corresponding to an arbitrary initial state of the system which might be given by

$$\psi = \Sigma c_n u_n$$

If the inequality (196') be satisfied, the product terms in the right hand sides of (219) or (219') vanish because they are formed from two different index values n and m. Therefore we directly get the measure of $|c_n|^2 A_{n,m}$ or $|c_n|^2 A_n(E')$ by measurement of $\epsilon - \epsilon'$ or $E' - \epsilon$ and E'. The complications arising out of the presence of the factors $A_{n,m}$ or $A_n(E')$ can be considered to be eliminated in that the colliding particle might be considered as being reflected here and back according undergoes further collisions and misses (?) its final total energy variation. This would be the case in which $|c_n|^2$ "Fällen" corresponds with a $E_n - E_m$ (m arbitrary), or in case of ionisation and simultaneous measurement of E' $E' - (\epsilon - \epsilon')$ would in $|c_n|^2$ "Fällen" coincide with E_n.

We can now schematise in general the measurement of the second kind with the help of the eigenfunction ψ of the measured system and the Ψ of the measuring apparatus. The state of the measuring apparatus, which is determinate, might correspond to the function system U_K (orthogonal, complete & normalised) In the above example the energy difference $\epsilon - \epsilon'$ is to be considered to take the place of K; since it makes no essential difference whether K be continuous

over K, even when one actually deals with an integral. If

$$\psi = \sum c_n u_n$$

be the state of the measured system before measurement (u_n are orthogonal & complete)

then

$$\sum \psi_k v_k$$

is the state of the total system after measurement, and on account of the linearity of the Hamilton function ψ_k must depend linearly on c_n:

$$\psi_k = \sum_n c_n \cdot v_k^{(n)} \qquad (220)$$

Thereby we have $\sum_k \int |\psi_k|^2 dQ = 1$ for all c_n, i.e. $\sum_k \int |v_k^{(n)}|^2 dq = 1$.

By "Ablesung" ( ) of a determinate R-value at the "apparatus" the wave-~~function~~ packet ψ is modified to the extent of a constant normalisation factor in the wave packet ψ_K. An unequivocal conclusion about c_n on the measured values of R is possible when and only when to each K there is only one unique $v_K^{(n)}$ different from zero. (To different K can however the same n may also belong). The state R can then be split up into groups such that each group belongs to a determinate value of n. We therefore write a double index n, m for K, and instead of (220)

$$\psi_{n,m} = c_n v_{n,m} \qquad (220')$$

Wherein from $\sum_n |c_n|^2 = 1$ for all c_n, the result

$$\sum_{n,m} \int |\psi_{n,m}|^2 dQ = 1$$

should follow. This is equivalent to

$$\int |v_n|^2 dQ = 1 \qquad (221)$$

The probability that the measurement is measuring apparatus is found in the group (n,m) with fixed n after the measurement must be equal to the probability that the system is in state n before measurement. Correspondingly therefore

$$|c_n|^2 = \sum_m \int |\psi_{nm}|^2 dq \qquad (222)$$

Naturally we can also develop the v_{nm} in terms of the u_n

$$v_{n,m} = \sum T_{l;n,m}\, u_l$$

For every (n,m) we have according to (220)

$$\sum_{l,m} |T_{l;n,m}|^2 = 1 \qquad (223)$$

This condition is plainly weaker than an orthogonality condition. For the measurements of the first kind $\underline{\underline{T}}$ is the special unit matrix. Also for the more general measurement of the second kind the special states, where $c_n = 1$ the rest $= 0$, have the property that an assertion with certainty can be made about them after the conclusion of the measurement. Thus: the measure result K will coincide in a determinate group with a predictable n.

We come back to the example of the energy-measurement of a system by collision. When we treat of excitation, we will assume that each energy-difference $E_n - E_m$ appears only for a particular pair of states. Then there is for each, ie for each $\epsilon - \epsilon'$, a unique E_n. Besides the v_{nm} are identical with the u_m except for a constant factor, and hence independent of n. In the case of the ionising

collision we think of the energy E' of the scattered electron also as measured by an apparatus, so that $\epsilon - \epsilon'$ and E' play together the role of K. To each K there is a unique n, determined by $E' - (\epsilon - \epsilon') = E_n$; while perhaps E' plays the role of m; v_{nm} is independent of n the eigen function for the continuous spectrum with the energy E'.

10. General formalism of perturbation theory: For many applications it is essential to possess a method of approximation for solving the wave equation which is applicable when the matrix elements of the energy are not all only diagonal, but the non-diagonal elements are however small as compared with the differences of the diagonal elements

$$H_{mn} \ll H_{mm} - H_{nn} \tag{224}$$

we shall confine ourselves to the case where a stationary solution of the wave equation is to be found, and introduce a complete orthogonal system $v_1, v_2 \ldots$ in which these conditions are satisfied. In this system the wave-equation for the stationary states is given by

$$\sum_n H_{mn} c_n = c_m E. \tag{225}$$

The eigen-function belonging to the energy E is then

$$u(E) = \sum c_n(E) v_n$$

since from $\underline{H} v_m = \sum_n v_n H_{nm}$

one has according to (225) the relation

If u be normalised, then when the v_n's are orthogonal and normalised we have

$$\sum |c_n|^2 = 1 \tag{226}$$

$$\left[\int u^* u \, dq = 1 = \sum c_n^* c_m^* \int v_n^* v_m \, dq = \sum |c_n|^2 \right]$$

From (225) it follows further that for different E we also have

$$\sum_n c_n(E)\, c_n(E') = 0 \quad \text{if} \quad E \neq E' \tag{226'}$$

$$\left[\sum_n H_{nn} c_n = c_n E \; ; \; \sum H_{nn}^* c_n^* = c_n E' \text{. Multiply first by } c_n^*(E')\, E', \text{ the second by } c_n(E)\, E \text{ and subtract. This gives regd. relation} \right]$$

If E be discrete, ie (225) can be solved only for discrete eigen-values $E_1, E_2, \ldots E_n$, we can write instead of $c_n(E_K)$

$$c_n(E_K) = S_{nK}$$

so that according to (226), (226') the S_{nK} form a unitary matrix. If we allow that K varies continuously in a certain region of values (perhaps many-dimensional), then the summation is to be replaced by an integral and we obtain the general case.

For the approximate solution of equations (225) we make the assumption that the non-diagonal elements are small as against the diagonal ones. To express this formally let us express the non-diagonal elements as multiplied by a parameter ϵ in terms powers of which c_n can be developed. We put

$$H_{nn} = E_n^{(0)} + \epsilon \Omega_{n,n} \; ; \; H_{nm} = \epsilon \Omega_{m,n}, \text{ for } n \neq m \tag{227}$$

And further search for a special solution which lies in the neighbourhood of

the eigen-values $E_K^{(0)}$ ie a coefficient system which in the zeroth approximation is equal to $\delta_{n,K}$:

$$\left.\begin{aligned} E_K &= E_K^{(0)} + \epsilon E_K^{(1)} + \epsilon^2 E_K^{(2)} + \dots \\ C_{n;K} &= \delta_{n,K} + \epsilon C_{n,K}^{(1)} + \epsilon^2 C_{n,K}^{(2)} + \dots \end{aligned}\right\} \qquad (228)$$

Equating in (225) and collecting different powers of ϵ

$$E_m^{(0)} C_{m,K}^{(1)} + \Omega_{m,K} = \delta_{m,K} E_K^{(1)} + C_{m,K}^{(1)} E_K^{(0)} \qquad (229_1)$$

[$\sum_n \delta_{nK} \Omega_{Km} = \Omega_{n,m}$ to be used here]

$$\left.\begin{aligned} E_m^{(1)} C_{m,K}^{(2)} + \sum_n \Omega_{m,n} C_{n,K}^{(1)} &= \delta_{m,K} E_K^{(2)} + C_{m,K}^{(1)} E_K^{(1)} + C_{m,K}^{(2)} E_K^{(0)} \\ &- - - - - - - - - - - - - \end{aligned}\right\} \qquad (229_2)$$

From (229_1) it follows for $m = K$, that

$$E_K^{(1)} = \Omega_{KK} \qquad (230)$$

ie <u>the variation of the Kth eigen-value is equal to the diagonal element (expectation value) of the perturbation energy in this state.</u> It also follows for $m \neq K$;

$$C_{m,K}^{(1)} \left[E_K^{(0)} - E_m^{(0)} \right] = \Omega_{m,K}$$

$$C_{m,K}^{(1)} = - \frac{\Omega_{m,K}}{E_m^{(0)} - E_K^{(0)}} \quad \text{for } m \neq K \qquad (231_1)$$

We see that the value of $C_{KK}^{(1)}$ remains undetermined. We have however to

Consider the normalisation condition, which developed in powers of ϵ gives

$$C^{(1)}_{KK} + C^{*(1)}_{KK} = 0 \qquad (232_1)$$

$$C^{(2)}_{KK} + C^{*(2)}_{KK} + \sum_n \left| C^{(1)}_{n,K} \right|^2 = 0 \qquad (232_2)$$

From the first of these equations it follows that $C^{(1)}_{KK}$ can be an arbitrary purely imaginary number. This indeterminacy arises from the fact that in the solution of (225) phase constants are entirely arbitrary. If $C_{n,K}$ is a solution so is

$$C'_{n,K} = C_{n,K}\, e^{i\delta_K}$$

with an arbitrary δ_K, and in order that this might not conflict with (228) it is only necessary to put

$$\delta_K = \epsilon \delta^{(1)}_K + \epsilon^2 \delta^{(2)}_K + \cdots$$

where $\delta^{(1)}_K, \delta^{(2)}_K \cdots$ are completely arbitrary.

Let us now go to a discussion of the second approximation. It follows from (229_2) first for $m = K$, and remembering (231_1) that

$$E^{(2)}_K = \sum{}' \Omega_{Kn} C^{(1)}_{n,K} = -\sum_n{}' \frac{\Omega_{Kn}\Omega_{nK}}{E^{(0)}_n - E^{(0)}_K} = -\sum{}' \frac{|\Omega_{Kn}|^2}{E^0_n - E^0_K} \qquad (230_2)$$

The accent over the summation indicates that the value $n = K$ is excluded. For the deepest eigen-value this energy eigenvalue perturbation is always negative. For $m \neq K$ it follows from (229_2)

$$C^{(2)}_{m,K}\left[E^0_m - E^0_K\right] = -\left(\Omega_{m,m} - \Omega_{KK}\right) C^{(1)}_{m,K} - \sum_n{}' \Omega_{m,n} C^{(1)}_{n,K}$$

$$c^{(2)}_{m,K} = \frac{(-\Omega_{m,m} - \Omega_{KK})\,\Omega_{m,K}}{(E^0_m - E^0_K)^2} + \sum_{n\,(n\neq m)}{}' \frac{\Omega_{m,n}\,\Omega_{n,K}}{(E^0_m - E^0_K)(E^0_n - E^0_K)} \quad (m \neq K); \qquad (231_2)$$

10]

$c^{(2)}_{KK}$ does not appear in these equations and must only satisfy the condition (232_2)

We can perhaps express these results more clearly by introducing the Hermitian matrix $\underline{\underline{T}}$ with the elements

$$T_{KK} = 0\,; \quad T_{m,K} = +\,i\,\frac{\Omega_{m,K}}{E^0_m - E^0_K} \quad (m \neq K) \qquad (233)$$

we then have

$$c^{(1)}_{m,K} = i\,T_{m,K} \quad \text{for } m \neq K \qquad (231_1')$$

$$E^{(2)}_K = \cancel{(T)}_{KK}\,(T-\Omega)_{K,K}. \qquad (232_2')$$

$$c^{(2)}_{m,K} = +\,i\,\frac{-\Omega_{m,m} - \Omega_{KK}}{E^0_m - E^0_K}\,T_{m,K} - (T^2)_{m,K} \quad (m \neq K) \qquad (231_2')$$

We notice here the theorem that an infinitesimal unitary matrix can always represented by a Hermitian matrix T multiplied by the imaginary unit i. If for example,

$$\underline{\underline{S}} = 1 + \epsilon\, i\, \underline{\underline{T}} \qquad (234)$$

so would the condition

$$S\tilde{S} = \tilde{S}S = 1$$

be equivalent to $T = \tilde{T}$ (ie T is Hermitian)

by neglection of higher powers of ϵ above the first. Corresponding to this result, according to (232_1) and $(231_1')$, $c^{(1)}_{Kn}$ is a Hermitian matrix except for

In (23), or in the equation above it in the summation $\sum'$

a term $C^{(1)}_{KK}$ appears, and this makes $C^{(2)}_{m,K}$ indeterminate even

$m \neq K$. This has got to be explained.

for a factor i.

[$C_{mK} = \delta_{nK} + \epsilon C^{(1)}_{m,K}$ is of the form $S = 1 + \epsilon T$, with $\overline{T_{mK}} = C^{(1)}_{mK} = i T_{mK}$

and $C^{(1)}_{KK} = i\alpha$]

From the form (231,) of $C^{(1)}_{mK}$ it can be shown by using (227) that condition (224) is in fact of decisive importance for the applicability of our approximation method. If this condition be not satisfied, the smallness of ϵ will not be satisfied since $\epsilon C^{(1)}_{m,K}$ would then be of the order of magnitude 1, and the procedure would not be justified. In particular this is true when the system is degenerate ie when many eigen-values $E_n^{(0)}$ exactly coincide. In this case it is necessary to consider first of all in particular the concerned finite dimensional subspace, and solve the eigenwerte problem

$$\sum_{n=1}^{g} H_{mn} c_n = c_m E \qquad (m = 1, 2 \cdots g) \tag{225'}$$

in the g-dimensional space in which $E_n^0 - E_m^0$ is of the same order of magnitude as H_{mn}. This is a purely algebraic problem and can always be solved, for eg one can determine g new eigen values E from the condition that the determinant (the so-called secular-determinant)

$$\begin{vmatrix} H_{11} - E & H_{12} & \cdots & H_{1g} \\ H_{21} & H_{22} - E & & H_{2g} \\ \cdots & & & \\ H_{g1} & H_{g2} & \cdots & H_{gg} - E \end{vmatrix} = 0 \tag{235}$$

vanishes, and this equation of order g for E has always g real roots for a Hermitian H_{mn}. After carrying out the transformation

$\bar{v}_m = \sum_n c_{n,m} v_n$ with the $c_{n,m}$ belonging to $E = E_m$ as determined from (225'), the $\bar{v}$'s may be adopted as the orthogonal system in which the perturbation function Ω may be denoted. This allows the application of the original approximation method to be followed. Because since after the transformation the $\Omega_{m,k}$ vanish when both m and k lie in the same sub-space, (231,) and (230$_2$) are again applicable. However the determinations $m \neq k$ or $n \neq k$ is to be understood in the following sense: The states m and k or n and k are to be belong to widely different non-degenerate energies (in different sub-spaces considered above). So that for this pair of states (224) is again satisfied.

We shall now indicate briefly as to how the above considered perturbation calculation is to be carried through if the concerned eigenvalues belong to the continuous spectrum. We consider instead of the index n, a continuous parameter n, so that

$$u(R) = \int c(n,K)\, v(n)\, dn$$

$$\underline{\underline{H}}\, v(m) = \int v(n)\, H(n,m)\, dm$$

$$\int H(m,n)\, C(n,K)\, dn = C(m,K)\, E(R),$$

Except that it depends on K, E is otherwise arbitrary, and is to be defined on grounds of usefulness. Instead of (227) we have to put

$$H(m,n) = E_n^0\, \delta(m-n) + \epsilon \Omega(m,n)$$

where we introduce the δ-functions defined in (145). Similarly

$$C(n,K) = \delta(n-K) + \epsilon\, C^{(1)}(n,K) + \epsilon^2 C^{(2)}(n,K) + \cdots ;$$

$$\left[E^0(m) - E^0(R)\right] C^{(1)}(m,k) = -\left[-\Omega(m,k) - E^{(1)}(R)\,\delta(m-k)\right]$$

On account of the appearance of the δ-function we can no longer specialise by taking $m = k$, and $E^{(1)}(R)$ remains arbitrary. In case $\Omega(m,k)$ has no singularity for $m = k$, or more precisely if $\int_{m-\epsilon}^{m+\epsilon} \Omega(m,k)\,dk$ vanishes for $\epsilon \to 0$, it is useful to put $E_k^{(1)} = 0$. We put accordingly

$$\Omega(m,k) - E^{(1)}(k)\,\delta(m-k) = \Omega'(m,k)$$

and require that

$$\lim_{\epsilon \to 0} \int_{m-\epsilon}^{m+\epsilon} \Omega'(m,k)\,dk = 0.$$

Then we have,

$$C^{(1)}(m,k) = -\frac{\Omega'(m,k)}{E_m^0 - E_k^0}$$

singular for $m = k$. A close discussion shows that for an integral

$$\int_{k-a}^{k+a} f(m)\,C^{(1)}(m,k)\,dm$$

where $f(m)$ is continuous but otherwise arbitrary it is permissible to substitute the principal value. This is defined by

$$\underline{\underline{H}} \int_{k-a}^{k+a} = \lim_{\epsilon \to 0}\left[\int_{k-a}^{k-\epsilon} + \int_{k+\epsilon}^{k+a}\right]$$

or also accordingly

$$\underline{\underline{H}} \int_{k-a}^{k+a} F(m,k)\,dm = \frac{1}{2}\int_{k-a}^{k+a}\left[F(m,k) + F(2k-m,k)\right] dm$$

where the integrand is regular. This is valid for the calculation of the $u(R)$ from

from the $v(n)$ with the aid of the $c(n,k)$ as also for the calculation of $E^{(2)}(k)$ and $C^{(2)}(n,k)$.

We now come to the consideration of time-dependent perturbations. For a given initial state ($t=0$) we want to find the solution of the wave equation

$$-\frac{\hbar}{i}\dot{c}_m = \sum_n H_{mn} c_n \tag{236}$$

[analogous to (225), and in fact obtained from it by taking $E \to -\frac{\hbar}{i}\frac{\partial}{\partial t}$]

where the matrix-elements of H related to a time-independent ~~system~~ orthogonal system are given by

$$H_{mn} = \delta_{m,n} E_n + \epsilon \Omega_{m,n}(t) \tag{237}$$

where the perturbation-matrix Ω might be an arbitrary function of the time.

The unperturbed solutions are

$$c_n^{(0)}(t) = c_n^{(0)}(0)\, e^{-\frac{i}{\hbar}E_n^0 t}, \text{ and}$$

we have to find the perturbed solutions

$$c_n(t) = c_n^{(0)}(t) + \epsilon c_n^{(1)}(t) + \epsilon^2 c_n^{(2)}(t) + \cdots$$

with prescribed values of $c_n(0) = c_n^0(0)$, so that also $c_n^{(1)}(0) = c_n^{(2)}(0) = \cdots = 0$. It is convenient to separate out the factor $e^{-\frac{i}{\hbar}E_n^0 t}$ from c_n and write

$$c_n(t) = a_n(t)\, e^{-\frac{i}{\hbar}E_n^0 t} \tag{238}$$

and also put,

$$\Omega'_{m,n}(t) = \Omega_{m,n}(t)\, e^{\frac{i}{\hbar}(E_m^0 - E_n^0)t} \tag{239}$$

Then we have,

$$-\frac{\hbar}{i}\dot{a}_m = \epsilon \sum_n \Omega'_{m,n}(t)\, a_n(t) \tag{237'}$$

and with $a_n(t) = a_n^{(0)}(t) + t\, a_n^{(1)}(t) + \cdots \quad \left(a_n^{(0)}(t) = a_n^{(0)}(0) = c_n^{(0)}(0) = \text{Const} \right)$

$$-\frac{\hbar}{i}\, \dot{a}_m^{(1)} = \sum_n \Omega'_{mn}(t)\, a_n^{(0)}(0)$$

$$-\frac{\hbar}{i}\, \dot{a}_m^{(2)} = \sum_n \Omega'_{m,n}(t)\, a_n^{(1)}(t).$$

These equations are immediately integrable

$$a_m^{(1)}(t) = -\frac{i}{\hbar} \sum_n a_n^{(0)}(0) \int \Omega'_{m,n}(t)\, dt \qquad (240_1)$$

$$a_m^{(2)}(t) = -\frac{i}{\hbar} \sum_l \int_0^t \Omega'_{m,l}\, a_l^{(1)}(t)\, dt$$

$$= -\frac{1}{\hbar^2} \sum a_n^{(0)}(0) \sum_l \int_0^t \Omega'_{ml}(\tau)\, d\tau \int_0^t \Omega'_{l,n}(\tau')\, d\tau' \qquad (240_2)$$

An important special case arises when $\Omega_{m,n}$ are independent of time. Then from (239),

$$\Omega'_{mn}(t) = \Omega_{m,n}(0)\, e^{\frac{i}{\hbar}(E_m^0 - E_n^0)t}$$

and (240) gives

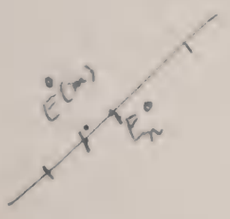
$$a_m^{(1)}(t) = -\sum_n a_n^{(0)}(0)\, \Omega_{m,n}(0)\, \frac{e^{\frac{i}{\hbar}(E_m^0 - E_n^0)t} - 1}{E_m^0 - E_n^0} \qquad (241_1)$$

$$a_m^{(2)}(t) = +\sum_n a_n^{(0)}(0) \sum_l \Omega_{ml}(0)\, \Omega_{l,n}(0) \left[\frac{e^{\frac{i}{\hbar}(E_m^0 - E_n^0)t} - 1}{(E_m^0 - E_n^0)(E_l^0 - E_n^0)} - \frac{e^{\frac{i}{\hbar}(E_m^0 - E_l^0)t} - 1}{(E_m^0 - E_l^0)(E_l^0 - E_n^0)} \right]$$

$$- \cdots (241_2)$$

If in (241_1) we have in particular $E_m^0 = E_n^0$, the corresponding term takes the form

$$a_n^0(0)\, \Omega_{m,n}(0)\, \frac{i}{\hbar}(t) \qquad [\text{Expanding } e^x]$$



und can be used as long as $|\epsilon|\,|\Omega_{m,n}(0)|\,\frac{t}{\hbar} \ll 1$. [In this case the second term in the expansion of $a_n(t) = a_n^0(t) + \epsilon a_n^{(1)}(t)$ will be small compared with the first]. If one wants to have in such a case corresponding to the vanishing of a denominator (resonance denominator) a solution which is valid for a longer time, one has to modify the perturbation process in an entirely analogous manner to the degenerate case or slightly degenerate case of stationary solutions.

A case which appears very often is that in which each discrete eigen-value of the unperturbed system lies in a region in which the system also possesses a continuous eigen-value spectrum. In such a case we can allow in (241,) the index n to take discrete values, and while m is the continuously varying index, and also take $\Omega_{m,n}$ as the matrix element normalised with respect to the parameter m. (The case where many parameters m appear is entirely analogous). In terms of probabilities we can then say that the system is transformed at time t into certain one of the states m for which

$$E_n^0 - \Delta E < E^0(m) < E_n^0 + \Delta E$$

when at time $t = 0$ it was certainly in the discrete state n ($a_n^{(0)}(0) = 1$; $a_n^0(m;0) = 0$). For this transition probability $W(t)$ we get

$$W(t) = \int |a^{(1)}(m,t)|^2\,dm = \int dm\,|\Omega_{mn}(0)|^2 \cdot \frac{4\sin^2\left[(E^0(m) - E_n^0)\frac{t}{2\hbar}\right]}{\left[E^0(m) - E_n^0\right]^2}$$

The integral is to be taken over any region of m-space which corresponds to the energy-interval $(E_n^0 - \Delta E,\ E_n^0 + \Delta E)$. When

$$\frac{\Delta E\, t}{\hbar} \gg 1 \qquad (242)$$

we can introduce

$$x = \frac{[E^0(m) - E_n^0]\, t}{2\hbar}$$

as the integration variable, and with sufficient approximation take $|\Omega_{mn}(0)|^2$ outside the integral (?) and integrate the remaining integral from $x = -\infty$ to $x = +\infty$ [from (242), $x \gg 1$]. In this way we get

$$W(t) = |\Omega_{mn}(0)|^2 \cdot \frac{t}{2\hbar} \frac{dm}{dE^0(m)} \cdot 4 \int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2}\, dx$$

$$\left[\text{Put } dm = \frac{dm}{dE^0(m)} \cdot dE^0(m);\ \frac{dE^0(m) \cdot t}{2\hbar} = dx \right]$$

and since the value of the integral is π, we have

$$W(t) = \frac{2\pi t}{\hbar} |\Omega_{m,n}(0)|^2 \frac{dm}{dE^0(m)} \qquad (243)$$

The factor $dm/dE^0(m)$ arises from the transition of the normalisation of the matrix elements of Ω with respect to m to the normalisation with respect to $E^0(m)$. If many parameters m, say m_1, m_2, m_3 appear, we have to consider the energy region $E_n^0 - \Delta E < E(m_1 m_2 m_3) < E_n^0 + \Delta E$ in the m-space. If this is given by

$$\int dm_1\, dm_2\, dm_3 = \omega(E_n^0)\, 2\Delta E \quad \left(E_n^0 - \Delta E < E(m_1 m_2 m_3) < E_n^0 + \Delta E\right)$$

the factor $\omega(E_n^0)$ appears in (243) in place of $dm/dE^0(m)$:

The eq^{n} (219) used in §9 is contained in the general form (241,). In this case the unperturbed system arises from two independent sub-systems so that the total energy appearing in (241,) is equal to the sum of the energies of both the parts so ie E_n^0 is to be replaced by $E_n + \epsilon$, $E^0(m)$ by $E_m + \epsilon'$ where E_n, E_m refer only to the atom, and ϵ, ϵ' to the colliding particle.

Just as we have considered here the initial state to be discrete, we might also consider it to be continuous. From (241) we again derive another formula of the type (243)

$$W_n(t) = \frac{2\pi t}{\hbar} \left| \Omega_{n,m}(0) \right|^2 \frac{dm}{dE^0(m)} P(m_0) \qquad (243')$$

where $P(m)\,dm$ denotes the density of the system in m-space. This means that when we consider a large number of systems, the fraction $P(m)\,dm$ have m-values between m and $m+dm$. further m_0 signifies specially the value of m, for which $E(m_0) = E_n^0$. Therefore it is averaged over all phases of $a_m^0(0)$ and in the considered interval $|a_m^0(0)|^2$ being independent of m, can be taken outside the integration with respect to m and put equal only $P(m_0)$ put in. On account of the Hermiticity of Ω, we always have $|\Omega_{m,n}(0)|^2 = |\Omega_{n,m}(0)|^2$ and this fact conditions according to (243) and (243') a relation an important relation, cerning the thermal equilibrium, about between a process and its reverse.

§11. Adiabatic and instantaneous perturbations of a system. The most general statement of probability in quantum mechanics.

A special case of an external influence on a system is one which can be described by varying a parameter. In the old quantum theory such an example was afforded by Ehrenfest's Adiabatic principle which states that a system, which is initially in a determinate stationary quantum state, remains in this state by the variation of a parameter of the system sufficiently slowly. That such a theorem is also true in wave mechanics was first formulated and proved by Born.

We consider accordingly a Hamiltonian operator $\underline{\underline{H}}$ dependent on a parameter $\underline{a}$, and assume the eigenvalue problem solvable for all values of a by means of the energy values $E_n(a)$ and the eigen-functions $u_n(a)$. Hence we have, identically in a, the equation

$$\underline{\underline{H}}\,(\underline{\underline{p}}, \underline{\underline{q}}, a)\, u_n(a) = E_n(a)\, u_n(a) \qquad (244)$$

Differentiation with respect to a gives

$$\left(\frac{\partial \underline{\underline{H}}}{\partial a}\right)_{\underline{\underline{p}},\underline{\underline{q}}} u_n(a) + \underline{\underline{H}}\,\frac{\partial u_n}{\partial a} = \frac{\partial E_n}{\partial a}\, u_n(a) + E_n \frac{\partial u_n}{\partial a} \qquad (244')$$

we now put

$$\frac{\hbar}{i}\int u_m^* \frac{\partial u_n}{\partial a}\, dq = K_{mn} \qquad (245)$$

where, on account of the orthogonality and normalisation of u, K_{mn}

is Hermitian. Further because of the Hermiticity of $\underline{\underline{H}}$

$$\frac{\hbar}{i}\int u_m^*\left(\underline{\underline{H}}\frac{\partial u_n}{\partial a}\right)dq = \frac{\hbar}{i}\int\left(\underline{\underline{H}}u_m\right)^*\frac{\partial u_n}{\partial a}\,dq = \frac{\hbar}{i}E_m K_{mn},$$

and multiflying (244') by $\frac{\hbar}{i}u_m^*$ and integrating over the q-space

$$\frac{\hbar}{i}\left(\frac{\partial\underline{\underline{H}}}{\partial a}-\frac{\partial\underline{\underline{E}}}{\partial a}\right) = \underline{\underline{k}}\,\underline{\underline{E}}-\underline{\underline{E}}\,\underline{\underline{k}} \qquad (246)$$

This is to be understood as a matrix equation in which $\underline{\underline{E}}$ is a diagonal matrix. In this case the diagonal elements of the right hand side vanish identically, and in particular it follows that

$$\left(\frac{\partial\underline{\underline{H}}}{\partial a}\right)_{n,n} = \frac{\partial E_n}{\partial a} \qquad (246')$$

and
$$K_{mn} = \frac{1}{E_n-E_m}\frac{\hbar}{i}\left(\frac{\partial\underline{\underline{H}}}{\partial a}\right)_{m,n} \quad \text{for } m\neq n\ (E_m\neq E_n) \qquad (246'')$$

If $\underline{a}$ is variable with time, we search for a solution of the equation

$$-\frac{\hbar}{i}\dot{\psi} = \underline{\underline{H}}\left(\underline{\underline{p}},\underline{\underline{q}},a\right)\psi$$

and with $\psi = \sum c_n(t)\,u_n(a)$

$$-\frac{\hbar}{i}\int u_m^*\dot{\psi}\,dq = \int u_m^*\left(\underline{\underline{H}}\psi\right)dq = E_m(a)\int u_m^*\psi\,dq$$

$$-\frac{\hbar}{i}\dot{c}_m + \dot{a}\sum k_{mn}c_n = E_m(a)\,c_m \qquad (247)$$

A closer examination of this equation shows that

$$c_m(T)-c_m(0) = \dot{a}F \qquad (248)$$

where for fixed finite $\dot{a}$ $T = a(T)-a(0)$ and $\lim T\to\infty$, accordingly

$\lim \dot{a} \to 0$, F remains finite. It is here assumed that during the process none of the differences $E_n - E_m$ pass through zero. This exceptional case is specially discussed by Born and Fock, wherein a conclusion arrived at by Lane plays an essential part. Also in this case, for fixed $a(T) - a(0)$

$$\lim_{\dot{a} \to 0} \left(c_m(T) - c_m(0) \right) = 0 \qquad (248')$$

from (248) it follows that $|c_m(T) - c_m(0)|^2$ is of order $\dot{a}^2$ for small $\dot{a}$.

In particular, for $c_m(0) = 0$ it follows that $|c_m(T)|^2 \sim \dot{a}^2$. The frequency of the transition from a stationary state to another which is brought about by variation of a parameter (Schüttelwirkung) is accordingly proportional to $\dot{a}^2$.

Perhaps a more general case than the one treated above is given when the parameter $\underline{a}$ brings about one more degree of freedom to the stat system. When for eg. an atom is moving in a spatial force field, we can consider the nucleus as fixed in the first approximation, and imagine the eigenvalue problem for every position Q of the centre of gravity of the atom solved

$$\underline{H_0}(q\,Q)\,u_n(q, Q) = E_n(Q)\,u_n \qquad (249)$$

Here Q does not vary with time but is to be considered as affording one more degree of freedom corresponding to this Q.

we have then to solve the equation

$$-\frac{\hbar}{i}\frac{\partial \psi}{\partial t} = \left(-\frac{\hbar^2}{2M}\sum_K \frac{\partial^2}{\partial Q_K^2} + \underline{\underline{H_0}}\right)\psi(q,Q) \qquad (250)$$

where $\underline{\underline{H_0}}$ acts only q and not on the Q. The same problem also appears for molecules when the nuclei are considered as fixed in the first approximation ($M = \infty$), and in the second approximation its motion (oscillation and rotation) are taken into account. We put

$$\psi(q,Q) = \sum_n \varphi_n(Q,t)\, u_n(q,Q) \qquad (251)$$

and hence according to (249)

$$-\frac{\hbar}{i}\sum \frac{\partial \varphi_n}{\partial t} u_n(q,Q) = \sum_n \left\{\left[-\frac{\hbar^2}{2M}\sum_K \frac{\partial^2 \varphi_n}{\partial Q_K^2} + E_n(Q)\varphi_n\right] u_n(q,Q)\right.$$

$$\left. -\frac{\hbar^2}{2M}\left[2\sum_K \frac{\partial \varphi_n}{\partial Q_K}\frac{\partial u_n}{\partial Q_K} + \varphi_n \sum \frac{\partial^2 u_n}{\partial Q_K^2}\right]\right\}$$

we introduce the hermitian matrices

$$A^{(K)}_{mn} = \frac{1}{M}\frac{\hbar}{i}\int u_m^* \frac{\partial u_n}{\partial Q_K}\, dq\,; \quad B_{mn} = -\frac{\hbar^2}{2M}\int u_m \sum_K \frac{\partial^2 u_n}{\partial Q_K^2}\, dq \qquad (252)$$

and for simplicity introduce a perturbation operator $\underline{\underline{Q}}$ defined by

$$\underline{\underline{Q}}\varphi_m = \sum_n \left(\sum_K A^{(K)}_{mn}\frac{\hbar}{i}\frac{\partial \varphi_n}{\partial Q_K} + B_{mn}\varphi_n\right) \qquad (253)$$

$$-\frac{\hbar}{i}\frac{\partial \varphi_m}{\partial t} = -\frac{\hbar^2}{2M}\sum_K \frac{\partial^2 \varphi_m}{\partial Q_K^2} + E_m(Q)\varphi_m + \underline{\underline{\Omega}}\,\varphi_m \qquad (254)$$

In particular there exist stationary solutions

$$\varphi_m(Q,t) = v_m(Q)\, e^{-\frac{i}{\hbar}Et}$$

for which

$$-\frac{\hbar^2}{2M}\sum \frac{\partial^2 v_m}{\partial Q_K^2} + E_m(Q)\, v_m + \underline{\underline{\Omega}}\, v_m = E v_m \qquad (254')$$

Here E can have either a discrete or continuous spectrum or a mixture of both.

Under certain circumstances the perturbation operator $\underline{\underline{\Omega}}$ can be considered small, and the usual perturbation method applied to (254) or (254'), as a result of which the zeroth approximation is

$$-\frac{\hbar}{i}\frac{\partial \varphi_m^0}{\partial t} = -\frac{\hbar^2}{2M}\sum_K \frac{\partial^2 \varphi_m^0}{\partial Q_K^2} + E_m(Q)\varphi_m^0 \qquad (255)$$

and

$$-\frac{\hbar^2}{2M}\sum_K \frac{\partial^2 v_m^0}{\partial Q_K^2} + E_m(Q)\, v_m^0 = E v_m^0 \qquad (255')$$

This method can be applied to the treatment of nuclear oscillation in a molecule as well as to the transition of an atom to another state due to a force field and other similar problems. We can denote this approximation as adiabatic because in this approximation the system stays in the same inner state m, and this is truer if the smaller is the variation of the packet φ_m^0 in comparison of the period $\hbar/[E_m(Q) - E_n(Q)]$, for eg in case of discrete spectra of

(255') the smaller are the energy differences $E' - E''$ of this ~~set~~ spectrum as compared with the differences $E_{n_1} - E_n$ of the spectrum of inner energy (smallness of nuclear oscillation frequencies relative to electron frequencies).

The equations (254) and (254') also constitute the basis for the transition in spatial directions of atomic rays due to magnetic fields. In this case it is sufficient to consider the states corresponding to the finite number of directional quantisations of the perturbation operator -2 in (253). From the strict existence of stationary solutions according to (254') it follows besides that the sum of the inner energy and translation energy remains constant under the action of "Schüttelwirkung" (as long as the external fields are not time variable).

Besides the limiting case of adiabatic process are also of special interest the "sudden" change of the parameter a. The term "sudden" is made precise by stating that the relative change of a in the period $\frac{1}{\nu_{nm}} = \frac{\hbar}{E_n - E_m}$ should be large:

$$\dot{a} \gg a \frac{E_n - E_m}{\hbar} \tag{256}$$

By integrating the equation

$$-\frac{\hbar}{i} \frac{\partial}{\partial t} \sum_n c_n u_n = \sum_m E_m c_m u_m$$

over the time duration of the change, we have

$$-\frac{\hbar}{i} \sum c_n [u_n(a)]_{t'}^{t} = \int_{t'}^{t} \sum E_m c_m u_m \, dt \; ;$$

ie in the first approximation all quantities proportional to t should be put equal to zero for a finite change of the parameter a. Since this is true for the right hand side of this equation it must be true for the left hand side also; ie

$$\sum_n C_n u_n = \sum C_n(0)\, u_n(0)$$

ie the continuity of the function $\psi = \sum c_n u_n$ for the instantaneous change of the parameter a

$$C_m(t) = \sum_n S_{mn} C_n(0) \qquad (257)$$

with $S_{mn} = \int u_m^*(a)\, u_n(0)\, dq.$

If H_{mn} are the matrix elements of the new Hamiltonian, which corresponds to value of the parameter a, in reference to the function-system belonging to $\underline{\underline{H}}(0)$,

$$H_{mn} = \int u_n^*(0)\, \underline{\underline{H}}(a)\, u_n(0)\, dq \qquad (258)$$

so that

$$\underline{\underline{E}}(a) = \underline{\underline{S}}\,\underline{\underline{H}}\,\underline{\underline{S}}^{-1} \qquad (259)$$

ie $\underline{\underline{S}}$ brings the matrix of the new Hamilton function to the diagonal form.

We can now discuss the most general form of the probability statements of quantum theory (for the sake of simplicity of writing we restrict ourselves to the discrete case). This can be formulated as follows: This is expressed by saying that $W(F_n; G_m)$ is the probability that at a determined

time t_1 a certain quantity F assumes the value F_n when at time $t_0 = t_1 - \tau$ an other quantity assumes the special value G_m. If S be the transformation matrix which leads to the representation in which $G(t_1)$ is brought to the diagonal form from the representation in which $F(t_0)$ is brought to the diagonal form, the required probability is given by

$$W(F_n ; G_m) = |S_{nm}|^2 \qquad (260)$$

(This is symmetrical with regard to magnitudes F and G). This statement is contained in our previous statements when (a) one or both of the magnitudes F and G is a position - or momentum variable, or (b) one or both of F and G is commutative with the Hamilton-function of the system and accordingly constant of the time.

If neither of these possibilities occur we can adopt, with the help of an artifice, a third possibility for the measurement depending on the "instantaneous" change of the Hamilton-function. The statement (260) is also true when (c) by varying a parameter it is possible to make the magnitude considered "instantaneously" a time-constant (ie to so alter the Hamiltonian as to make the magnitude commute with it ("Stör-annahme")). In this case we can first make F time-constant at t_0 and measure it, and then after time τ at the end of the measurement make G time-constant and measure it. From the above mentioned results

validity of (260) for this case.

It must however be emphasized that this sudden stopping of a magnitude is possible only in a limited circle. For eg it is impossible to suddenly "abzuschalten" the nuclear charge of the proton, and to make the momentum of the electron in the H-atom instantaneously a time-constant. In this case the determination of the eigenfunction $\varphi_n(p)$ in momentum spaces is reached by a measurement of the second kind in which a repitition of the measurement gives a different result (possibility (60)). It is however not generally proved that, when measurements of the second kind are allowed, every quantity can be measured in an arbitrarily short interval of time.

on the basis of these ideas we see that (260) is not be introduced as an axiom in contradistinction with the dogmatic foundations of the transformation theory. In the last analysis the possibility of measurement of a magnitude comes back to the measurement of position by an apparatus. An apparatus measures a quantity F when by splitting the ψ-function into normalised orthogonal functions u_n of the operator $\underline{F}$ corresponding to F, the apparatus indicates with certainty the "scale readings" $Q_1, Q_2 \ldots Q_n$ if before the measurement ψ was in particular equal to $u_1, u_2 \ldots u_n \ldots$ In the general case the probability for the scale-reading Q_n is to be defined

as the probability that the quantity F has the value F_n before the measurement. From the significance of the ψ-function of the apparatus, and the linearity of all Hamiltonian operators it then follows that this probability is equal to the square of the modulus of the coefficient in the development of the ψ-function of the system before measurement in terms of the functions u_n ($\mathfrak{F}_n = \int u_n^* \psi_n \, dq$). If further later a new measurement of another quantity G is made by a new apparatus which is described by the scale readings $Q_1, Q_2 \ldots$, the probability that the new G has a certain value G_m, when earlier F has certainly the value F_n, is defined as identical with the probability that the new apparatus indicates the scale reading Q_m when it is well known that the first apparatus has certainly the scale reading Q_n, so that this time one might have a unique conclusion about the state of the system after measurement (which for measurements of the second is not the same as the state before). The last statement is identical with this that the state of the measured system after the first measurement is describable by the eigen-functions u_n.

Let $v_1, v_2 \ldots v_m \ldots$ be the eigen-functions of the quantity G; the probability $W(F_n, G_m)$ is in fact equal to $|S_{nm}|^2$ where $S_{nm} = \int u_n v_m^* \, dq$.

Therefore it appears that all assertions about arbitrary magnitudes F, G, ... come back to corresponding probability assertions about the

scale-readings of apparatus, and accordingly to position-probabilities. We however leave it open as to whether or not there actually exist apparatus with the postulated conditions for arbitrary F and G. ~~Thus~~ Because this question is dependent on the question as to what Hamiltonian functions actually appear in nature, and non-relativistic quantum-mechanics can make no statements about this. The concepts and formalism of this non-relativistic theory are so general that it would be still free from contradictions even if we assume arbitrary (Hermitian) Hamiltonian operators.

§ 12. Transition to classical mechanics. Relation to the old quantum theory.

In § 5 we have already given a relation between the wave-mechanical equation, and classical mechanics viz that the centre of a wave packet moves like a particle acted on by a force equal to the mean value of the classical force over the packet. This does not really signify any complete limiting transition to classical mechanics since the classical force might vary very much along the wave packet, and therefore the mean value of the classical force may deviate ~~very~~ arbitrarily strongly from the its value at the centre of the wave packet. Infact we obtain complete ~~corresponding~~ correspondence with the properties of the system depending on their classical orbits only when we can construct

wave packets inside which the classical force varies but slightly and also when we consider such times during which the dimensions of the wave packet only slightly varies. Considering the case of stationary ~~and~~ states and periodic orbits, it is necessary that this time should be at least more than the periodic time of revolution, so that the properties of the stationary states in the wave packet in so far as they differ relatively slightly from each other can be approximately described with the help of the classical representation by orbits.

The limiting transition from wave mechanics to classical mechanics is formally analogous to the transition from wave optics to geometrical optics (Hamilton), and this analogy was even used as the starting point of the considerations of de Broglie and Schrödinger on the representation of wave mechanics. ~~When~~ ~~to~~ In the general wave equation

$$-\frac{h}{i}\frac{\partial \psi}{\partial t} = H\psi$$

~~One~~ makes the substitution

$$\psi = e^{\frac{i}{h}S} \quad ; \qquad (261)$$

and then develops S in increasing powers of h/i:

$$S = S_0 + \left(\frac{h}{i}\right) S + \left(\frac{h}{i}\right)^2 S_2 + \cdots \qquad (262)$$

We first of all consider the Hamiltonian operator in cartesian coordinates

(See for eq. (97), (98) where we suppose the $V^{(a)}$ included in $V(q_1 \cdots q_f)$)

$$\underline{H} = \sum \frac{1}{2m_k} \left(\frac{\hbar}{i} \frac{\partial}{\partial q_k} + A_k \right)^2 + V$$

where the $A_k = -\frac{e_k}{c} \Phi_k$ and V are arbitrary real functions of q. According to (261) we have first of all

$$\left(\frac{\hbar}{i} \frac{\partial}{\partial q_k} + A_k \right) e^{\frac{i}{\hbar} S} = \left(\frac{\partial S}{\partial q_k} + A_k \right) e^{\frac{i}{\hbar} S}$$

$$\left(\frac{\hbar}{i} \frac{\partial}{\partial q_k} + A_k \right)^2 e^{\frac{i}{\hbar} S} = \left[\left(\frac{\partial S}{\partial q_k} + A_k \right)^2 + \frac{\hbar}{i} \left(\frac{\partial^2 S}{\partial q_k^2} + \frac{\partial A_k}{\partial q_k} \right) \right] e^{\frac{i}{\hbar} S} \quad [* \text{ P.T.O}$$

The wave equation now gives, after the factor $e^{\frac{i}{\hbar} S}$ taken out, without any neglection

$$-\frac{\partial S}{\partial t} = \sum_k \frac{1}{2m_k} \left[\left(\frac{\partial S}{\partial q_k} + A_k \right)^2 + \frac{\hbar}{i} \frac{\partial}{\partial q_k} \left(\frac{\partial S}{\partial q_k} + A_k \right) \right] + V \qquad (263)$$

Now using the series development (262) we have finally the successive equations

$$-\frac{\partial S_0}{\partial t} = \sum_k \frac{1}{2m_k} \left(\frac{\partial S_0}{\partial q_k} + A_k \right)^2 + V = H \left(\frac{\partial S_0}{\partial q_k}, q_k \right) \qquad (264_0)$$

where in the Hamilton function p_k is simply substituted by $\partial S_0 / \partial q_k$.

Further we have

$$-\frac{\partial S_1}{\partial t} = \sum_k \frac{1}{2m_k} \left[2 \left(\frac{\partial S_0}{\partial q_k} + A_k \right) \frac{\partial S_1}{\partial q_k} + \frac{\partial}{\partial q_k} \left(\frac{\partial S_0}{\partial q_k} + A_k \right) \right] \qquad (264_1)$$

Instead of (264_1) we can also write

$$-\frac{\partial}{\partial t} e^{2S_1} = \sum_k \frac{\partial}{\partial q_k} \left[\frac{1}{m_k} \left(\frac{\partial S_0}{\partial q_k} + A_k \right) e^{2S_1} \right] \qquad (265)$$

The equations (264_0) and (265) have a simple physical significance.

$$
\begin{aligned}
* \quad & \left(\frac{\hbar}{i}\frac{\partial}{\partial q_K} + A_K\right)\left(\frac{\hbar}{i}\frac{\partial}{\partial q_K} + A_K\right) e^{i/\hbar S} \\
&= \left(\frac{\hbar}{i}\frac{\partial}{\partial q_K} + A_K\right)\left(\frac{\partial S}{\partial q_K} + A_K\right) e^{i/\hbar S} \\
&= \frac{\hbar}{i}\frac{\partial}{\partial q_K}\left(\frac{\partial S}{\partial q_K} + A_K\right) e^{i/\hbar S} + A_K\left(\frac{\partial S}{\partial q_K} + A_K\right) \\
&= \left(\frac{\partial S}{\partial q_K} + A_K\right)\frac{\partial S}{\partial q_K} e^{i/\hbar S} + \left(\frac{\hbar}{i}\frac{\partial^2 S}{\partial q_K^2} + \frac{\partial A_K}{\partial q_K}\right) e^{i/\hbar S} + A_K\left(\frac{\partial S}{\partial q_K} + A_K\right) e^{i/\hbar S} \\
&= \left(\frac{\partial S}{\partial q_K} + A_K\right)^2 e^{i/\hbar S} + \left(\quad " \quad \right).
\end{aligned}
$$

The first is the well-known Hamilton-Jacobi partial differential equation of classical mechanics. It is to noticed that the solutions of this equation in the region which can be attained by the considered mechanical trajectories are all real. According to (264,) S_1 is also real in this region Under the assumption of the real characters of S_0 and S_1, (265) (neglecting S_2 etc..) is ~~not~~ identical with the continuity equation. In fact putting

$$\rho = \psi^* \psi = e^{2S_1}$$

$$i_K = \frac{1}{2m_K}\left[\psi^*\left(\frac{\hbar}{i}\frac{\partial \psi}{\partial q_K} + A_K \psi\right) + \psi\left(-\frac{\hbar}{i}\frac{\partial \psi^*}{\partial q_K} + A_K \psi^*\right)\right] = \frac{1}{m_K}\left(\frac{\partial S_0}{\partial q_K} + A_K\right) e^{2S_1}$$

on account of

$$\dot{q}_K = \frac{\partial H}{\partial p_K} = \frac{1}{m_K}\left(\frac{\partial S_0}{\partial q_K} + A_K\right) \tag{266}$$

we have

$$i_K = \rho \dot{q}_K \tag{267}$$

and (265) takes the form

$$\frac{\partial \rho}{\partial t} + \sum_K \frac{\partial}{\partial q_K}(\rho \dot{q}_K) = 0 \tag{265'}$$

which corresponds to the continuity equation. We construct ~~accordingly~~ a mechanical trajectory, according to (266), through the point of q-space at which S_0 is real, and according to (265') the density remains a time-constant along this trajectory. (when the solution of S_0 in (264$_0$) contains no parameter there is one trajectory and in the general case there is one determinate path for every special determinate value of the parameters $\alpha_1, \alpha_2 \ldots$ appearing in S_0. In the considered

approximation the wave packet behaves exactly like a totality of particles which move along the classical orbit. That these particles also satisfy the second half

$$\dot{p}_k = -\frac{\partial H}{\partial q_k}$$

of the classical equations of motion, is a simple consequence of (264$_0$) and (266) as is well-known from the Hamilton-Jacobi theory.

[$p_k = \frac{\partial S}{\partial q_k}$ because of the contact transformation theory, and

$\dot{p}_k = \frac{\partial}{\partial t}\left(\frac{\partial S}{\partial q_k}\right)$, since $\sum \frac{\partial}{\partial q_j}\left(\frac{\partial S}{\partial q_k}\right)\dot{q}_j = 0$. From the H-J eq. $\frac{\partial}{\partial t}\left(\frac{\partial S}{\partial q_k}\right) = \frac{\partial}{\partial q_k}\left(\frac{\partial S}{\partial t}\right) = -\frac{\partial H}{\partial q_k}$]

Concerning the region of validity of the approximation considered here we observe that this can be characterized with the aid of (263) by saying that the term in (263) multiplied by $\hbar/i$ should be small compared with the first term. Putting for shortness

$$\Pi_k = \frac{\partial S}{\partial q_k} + A_k = p_k + A_k = m_k \dot{q}_k \qquad (266a)$$

this condition means that

$$\hbar \sum \frac{\partial \Pi_k}{\partial q_k} \ll \sum \Pi_k^2 \qquad (268)$$

In the case of absence of a magnetic field, and a single particle this becomes we have

$$\Pi_k = p_k = \frac{\hbar}{i} n_k$$

where n_k is the component of a unit vector in the direction of motion. Further

case (268) assumes the special form

$$\lambda^2 \sum_k \frac{\partial}{\partial q_k}\left(\frac{n_k}{\lambda}\right) \ll 1$$

or

$$\sum_k \left(\lambda \frac{\partial n_k}{\partial q_k} - n_k \frac{\partial \lambda}{\partial q_k}\right) \ll 1 \qquad (268')$$

In the one-dimensional problem where $n_k = \pm 1$, this becomes finally the simple expression

$$\left|\frac{\partial \lambda}{\partial x}\right| \ll 1 \qquad (268'')$$

The inequality (268) is in general not satisfied at the turning points where one of the π_k's, accordingly $\dot{q}_k$ also, vanishes and since at that point $\partial \pi_k / \partial q_k$ might be infinite, as is always the case in particular for the one-dimensional problem. In the neighbourhood of this point classical mechanics is not valid, and it is necessary to have a special investigation for the behaviour of the solution near this point, and this will be done later. Further, the equations (264) and (265) might be applicable in regions where not attainable by classical mechanics in virtue of S_0 being imaginary, for in the setting up of these equations no assumptions are made regarding reality character of the solutions.

For a stationary solution

$$\psi = e^{\frac{-i}{\hbar} Et} u$$

$$S = -Et + \bar{S}, \quad u = e^{\frac{i}{\hbar}\bar{S}}$$

where, now, $\bar{S}$ and u are independent of t. With

$$\bar{S} = \bar{S}_0 + \frac{\hbar}{i}\bar{S}_1 + \cdots \qquad (262')$$

(264) and (265) would be

$$\sum_k \frac{1}{2m_k}\left(\frac{\partial \bar{S}_0}{\partial q_k} + A_k\right)^2 + V = H\left(\frac{\partial \bar{S}_0}{\partial q_k}, q_k\right) = E \qquad (264_0')$$

$$0 = \sum_k \frac{1}{2m_k}\left[2\left(\frac{\partial \bar{S}_0}{\partial q_k} + A_k\right)\frac{\partial \bar{S}_1}{\partial q_k} + \frac{\partial}{\partial q_k}\left(\frac{\partial \bar{S}_0}{\partial q_k} + A_k\right)\right] \qquad (264_1')$$

$$0 = \sum_k \frac{\partial}{\partial q_k}\left[\frac{1}{m_k}\left(\frac{\partial \bar{S}_0}{\partial q_k} + A_k\right)e^{2\bar{S}_1}\right] \qquad (265')$$

It is easy to generalise the previous results to the case of curvilinear coordinates q if

$$ds^2 = \sum_\varkappa \sum_\lambda g_{\varkappa\lambda}\, dq_\varkappa\, dq_\lambda$$

be the line-element, and $g^{\varkappa\lambda}$ the determinant reciprocal to $g_{\varkappa\lambda}$ ($g_{\varkappa\alpha}\, g^{\lambda\alpha} = \delta_\varkappa^\lambda$), D the square root of the determinant $g = |g_{\varkappa\lambda}|$ the wave equation is

$$-\frac{\hbar}{i}\frac{\partial \psi}{\partial t} = \frac{1}{2D}\left(\frac{\hbar}{i}\frac{\partial}{\partial q_\varkappa} + A_\varkappa\right) D g^{\varkappa\lambda}\left(\frac{\hbar}{i}\frac{\partial}{\partial q_\lambda} + A_\lambda\right)\psi + V\psi$$

we shall assume the factors $m_\varkappa$ included in $g_{\varkappa\lambda}$ and also adopt the summation convention. The substitution (261) then gives

$$-\frac{\partial S}{\partial t} = \frac{1}{2} g^{\varkappa\lambda}\left(\frac{\partial S}{\partial q_\varkappa} + A_\varkappa\right)\left(\frac{\partial S}{\partial q_\lambda} + A_\lambda\right) + \frac{1}{2}\cdot\frac{1}{D}\frac{\hbar}{i}\frac{\partial}{\partial q_\varkappa} D g^{\varkappa\lambda}\left(\frac{\partial S}{\partial q_\lambda} + A_\lambda\right) + V \qquad (263^*)$$

Substituting the development (262) and (remembering $g^{\chi\lambda} = g^{\lambda\chi}$)

$$-\frac{\partial S_0}{\partial t} = \frac{1}{2} g^{\chi\lambda}\left(\frac{\partial S_0}{\partial q_\chi} + A_\chi\right)\left(\frac{\partial S_0}{\partial q_\lambda} + A_\lambda\right) + V = H\left(\frac{\partial S_0}{\partial q_\chi}, q_\chi\right) \qquad (264_0^*)$$

$$-\frac{\partial S_1}{\partial t} = g^{\chi\lambda}\left(\frac{\partial S_0}{\partial q_\chi} + A_\chi\right)\frac{\partial S_1}{\partial q_\lambda} + \frac{1}{2}\frac{1}{D}\frac{\partial}{\partial q_\chi} D g^{\chi\lambda}\left(\frac{\partial S_0}{\partial q_\lambda} + A_\lambda\right) \qquad (264_1^*)$$

or

$$-\frac{\partial}{\partial t} e^{2S_1} = \frac{1}{D}\frac{\partial}{\partial q_\chi}\left[D g^{\chi\lambda}\left(\frac{\partial S_0}{\partial q_\lambda} + A_\lambda\right) e^{2S_1}\right] \qquad (265^*)$$

with

$$\rho = D\psi\psi^*, \quad i^\chi = D g^{\chi\lambda}\left[\psi^*\left(\frac{\hbar}{i}\frac{\partial \psi}{\partial q_\lambda} + A_\lambda \psi\right) + \psi\left(-\frac{\hbar}{i}\frac{\partial \psi^*}{\partial q_\lambda} + A_\lambda \psi^*\right)\right]$$

The continuity equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial q_\chi} i^\chi = 0 \text{ , from the general equation ,}$$

and for real S_0 and S_1 we would have in the considered approximation

$$\rho = e^{2S_1}$$

$$\dot{q}^\chi = \frac{\partial H}{\partial p_\chi} = g^{\chi\lambda}\left(\frac{\partial S_0}{\partial q_\lambda} + A_\lambda\right) \qquad (266^*)$$

$$i^\chi = \rho \dot{q}^\chi \qquad (267^*)$$

Wherefrom can be drawn the same conclusions as done earlier for the classical cartesian coordinates.

The introduction of curvilinear coordinates is important in that sometimes for special Hamiltonian functions the variables of the

as the product of functions of several variables

$$u = u_1(q_1) \cdots u_f(q_f)$$

and correspondingly $\bar{S}$ splits up additively to

$$\bar{S} = \bar{S}_1(q_1) + \bar{S}_2(q_2) + \cdots + \bar{S}_f(q_f).$$

Each of these functions $\bar{S}_x(q_x)$ then satisfies a differential equation of the second order in these variables in which however besides the energy-constant there appear $f-1$ further constants $\alpha_2 \cdots \alpha_f$ also appear. All that was mentioned above for systems of one degree of freedom follows mutatis mutandis follows also for the motion of each separation-coordinate q_x and the corresponding eigen-functions $u_x(q_x)$ of the separable systems. In particular this is the case for the motion of a particle under the influence of a central force.

We will now consider the one dimensional case more exactly. Here it is necessary to put the vector potential equal to zero since the magnetic field does not enter in the one dimensional case. Let us consider the stationary case and replace for simplicity $\bar{S}_0$ by S and $e^{\bar{S}_1}$ by a so that in the approximation considered

$$u = a e^{\frac{i}{\hbar} S}$$

and (264') and (265') become

$$\frac{1}{2m}\left(\frac{dS}{dx}\right)^2 + V(x) = E \qquad (269)$$

$$0 = \frac{d}{dx}\left(a^2 \frac{dS}{dx}\right) \qquad (270)$$

accordingly with

$$p(x) = \sqrt{2m\,(E - V(x))} = \pm \frac{dS}{dx} \tag{271}$$

$$S = \pm \int^{x} p(x)\,dx$$

where we shall prescribe the lower limit later and the double sign corresponds to two different particular solutions of (269). So that it follows that

$$a^2 \frac{dS}{dx} = \text{const} = C^2$$

$$a = \frac{C}{\sqrt{p(x)}} = \frac{C}{\sqrt{2m\,(E - V(x))}} \tag{272}$$

The general solution of (269) and (270) reads accordingly

$$u = \frac{C_1}{\sqrt{p(x)}}\, e^{\pm \frac{i}{\hbar} \int_{a_1}^{x} p(x)\,dx} + \frac{C_2}{\sqrt{p(x)}}\, e^{-\frac{i}{\hbar} \int_{a_2}^{x} p(x)\,dx} \tag{273}$$

It breaks down in the neighbourhood of points where $p(x)$ vanishes. Also in the regions where $E - V(x)$ is negative & $p(x)$ is accordingly purely imaginary there exists a solution of the form (273) which cannot be reached classically. In this region we therefore write for the sake of clearness the form

$$u = \frac{C_1'}{\sqrt{|p(x)|}}\, e^{-\frac{1}{\hbar} \int_{a_1}^{x} |p(x)|\,dx} + \frac{C_2'}{\sqrt{|p(x)|}}\, e^{+\frac{1}{\hbar} \int_{a_2}^{x} |p(x)|\,dx} \tag{273'}$$

The consideration of the differential equations (269) and (270) of geometrical optics (classical mechanics) alone are not sufficient to bring together the particular solutions (273) and (273') correctly at the critical points, the turning points with $p(x) = 0$. Since by "correctly" it is here understood that the different particular

solutions of (269), (270) should approximate to the same particular solution $u(x)$ of the rigorous wave equation

$$\hbar^2 \frac{d^2u}{dx^2} + p^2(x)\, u = 0$$

in the different regions where $p^2(x) > 0$ and $p^2(x) < 0$, it is imperative to draw upon the rigorous wave equation at least in the neighbourhood of the turning point.

The not too simple mathematical question that crops up here has been completely investigated by Kramers and his school. The result is the following: We assume that $V(x)$ is continuous at the turning point (this makes it possible to make use of the complex plane in the proof). Let further to the right of the turning point $x = a$ i.e. for $x > a$, $p^2(x) > 0$, and for $x < a$, $p^2(x) < 0$. Then according to Kramers

$$\left.\begin{aligned} u(x) &= \frac{C}{\sqrt{|p(x)|}}\, e^{-\frac{1}{\hbar}\int_x^a |p(x)|\,dx} && \text{for } x < a \\ u(x) &= \frac{C}{\sqrt{p(x)}}\, 2\cos\left[\frac{1}{\hbar}\int_a^x p(x)\,dx - \frac{\pi}{4}\right] && \text{for } x > a \end{aligned}\right\} \qquad (274)$$

is a "correct" correspondence. In general correspond

$$\left.\begin{aligned} u(x) &= \frac{C}{i\sqrt{|p(x)|}}\, e^{+\frac{1}{\hbar}\int_x^a |p(x)|\,dx} + \frac{1}{2}\,\frac{C}{\sqrt{|p(x)|}}\, e^{-\frac{1}{\hbar}\int_x^a |p(x)|\,dx} && \text{for } x < a \\ u(x) &= \frac{C}{\sqrt{p(x)}}\, e^{i\left[\frac{1}{\hbar}\int_a^x p(x)\,dx - \frac{\pi}{4}\right]} && \text{for } x > a \end{aligned}\right\} \qquad (275)$$

Forming the real parts of both the expressions in (275), which is permissible, we come back to the correspondence (274). From the imaginary parts also we can form

equally a correct correspondence. It is suitable that the second term in the first expression of (275) is so small compared with the first that it falls within the limit of error of the complete asymptotic representation and can be omitted for many purposes. For all questions however where not only the modulus of $u(x)$ but also its phase plays a part it is necessary to retain it; in particular is this so ~~for~~ in ~~ordered to~~ order that the current formed for $x < a$ should be the same as for $x > a$ as required by the continuity equation.

For a second turning point $b > a$ which has the allowed region to its left we have the correspondence analogous to (274)

$$\left.\begin{aligned} u(x) &= \frac{C'}{\sqrt{|p(x)|}}\, e^{-\frac{1}{\hbar}\int_b^x |p(x)|\,dx} \qquad \text{for } x > b \\ u(x) &= \frac{C'}{\sqrt{p(x)}}\, 2\cos\left[\frac{1}{\hbar}\int_x^b p(x)\,dx - \frac{\pi}{4}\right] \qquad \text{for } x < b \end{aligned}\right\} \tag{275'}$$

We can now specify the quantum conditions for the case of the region $p^2(x) > 0$ for which the concerned energy eigenvalue E arises from a single indecomposed interval $a < x < b$. We shall expressly make this an assumption. Since $u(x)$ is bounded for $x = -\infty$ as well as for $x = +\infty$, the particular solutions arising from the exponentials should be absent for both the regions $x < a$ and $x > b$ and only the degenerate (besides very sharp) solutions alone should appear. For this it is necessary according to (275) and (275') that for all x in the interval $a < x < b$

$$\frac{1}{\hbar}\int_x^b p(x)\,dx - \frac{\pi}{4} = \left(n + \frac{1}{2}\right)\pi$$

This is only possible if the (constant) sum of the two phases is a multiple of π:

$$\frac{1}{\hbar}\int_a^b p(x)\,dx - \frac{\pi}{2} = n\pi$$

or with

$$J = 2\int_a^b p(x)\,dx = \oint p(x)\,dx \qquad (276)$$

$$\frac{1}{\hbar} J = \left(n+\tfrac{1}{2}\right) 2\pi\,, \quad J = \left(n+\tfrac{1}{2}\right) h \qquad (277)$$

Besides we also have

$$C' = (-1)^n C$$

This corresponds to the fact that n denotes the number of nodes of the eigenfunction in fact as the phase increases from

$$\frac{1}{\hbar}\int_a^x p(x)\,dx - \frac{\pi}{4}$$

increases from $-\frac{\pi}{4}$ to $\left(n+\frac{1}{2}\right)\pi - \frac{\pi}{4}$, when x varies from a to b, the cosine assumes n times its original value.

The result (277) leads to the rule of quantisation of the old quantum theory but with "half-integral quantisation": ie the phase integral of the old quantum theory would be a half-integral multiple of h. This shows accordingly that we get a better approximation by wave mechanics than when one has integral quantisation. According to previous statements the same is true for the case of more than one degree of freedom when separation of variables is permissible. Here we have however specially assumed that the concerned degree of freedom is of the oscillation type ie that to every value of the coordinate q_1 in a definite interval

there correspond two values of the velocity $\dot{q}$ of the particle equal but opposite in sign so that each point is described twice in a complete period, while the q-point outside the concerned region cannot be reached by any mechanical orbit with the same values of the integration constants. In contrast to the oscillation type we have the rotational type of degree of freedom for eg a cyclical angular coordinate (precessional motion about a fixed axis). We will see that in this case (so long as one deals only with the orbital motion but not the spin of a particle) wave mechanics leads to integral quantisation.

If there appear more than one interval which can be reached by classical orbits with the same total energy, there appear peculiar wave mechanical effects which depend on this that according to (275) the wave function is not zero in the regions inaccessible classically but but is only very small. While classically two regions are completely separated by a "potential hill" of finite height for a particle of definite energy, the wave function can "creep through" from one region to another and the wave stationary solution would have sensibly the same density in both the regions. This situation is of fundamental significance for numerous applications of quantum theory. We will consider it again in Part B, §5 in the relativistic quantum theory.

As far as the condition (268") is concerned we notice that it is satisfied better the larger the quantum number n. We can now normalise our eigenfunctions wherein we notice that for large quantum numbers the phase

the phase

$$\frac{1}{\hbar}\int_a^x p(x)\,dx - \frac{\pi}{4}$$

is a rapidly varying function and hence we can neglect such integrals which contain rapidly varying phases in comparison with those which contain only slowly varying or non-oscillating phases. In this approximation the eigen-functions are also orthogonal. By normalisation we obtain the condition

$$4C^2\int_a^b \frac{dx}{p(x)}\cos^2\left[\frac{1}{\hbar}\int_a^x p(x)\,dx - \frac{\pi}{4}\right] = 1$$

or

$$2C^2\int_a^b \frac{dx}{p(x)} = 2C^2\int_a^b \frac{dx}{m\dot{x}} = \frac{C^2}{m\omega} = 1$$

where (according to the definition (276) of the phase integral J)

$$\frac{1}{\omega} = 2\int_a^b \frac{dx}{\dot{x}} = 2m\int_a^b \frac{dx}{\sqrt{2m(E-V(x))}} = \frac{\partial J}{\partial E} \qquad (278)$$

denotes the period of the classical motion. Accordingly

$$u_n(x) = \sqrt{\frac{m\omega_n}{p_n(x)}}\,2\cos\left[\frac{1}{\hbar}\int_{a_n}^x p_n(x)\,dx - \frac{\pi}{4}\right] \qquad (279)$$

is the normalised eigen-function. We form the matrix x_{nm}

$$x_{nm} = \int x\,u_n u_m\,dx = \int x\sqrt{\frac{m\omega_n}{p_n(x)}}\sqrt{\frac{m\omega_m}{p_m(x)}}\,2\left\{\cos\left[\frac{1}{\hbar}\int_{a_n}^x p_n(x)\,dx - \frac{1}{\hbar}\int_{a_m}^x p_m(x)\,dx\right]\right.$$
$$\left. + \cos\left[\frac{1}{\hbar}\int_{a_n}^x p_n(x)\,dx + \frac{1}{\hbar}\int_{a_m}^x p_m(x)\,dx - \frac{\pi}{2}\right]\right\}dx$$

Since the second term, which contains the sum of the phases, oscillates much more rapidly than the first term which contains the difference of the phases, we can

we can neglect the former. Further all quantities vary slowly with the quantum number so that we can replace all differences of the form $F_n - F_m$ by the differential coefficients $\frac{\partial F}{\partial J}(n-m)h$, where J again denotes the phase integral defined by (276). The differentiation with respect to the lower limit of the integral $\int_a^x p(x)\,dx$ gives no contribution since the integrand vanishes at that limit. In this manner we have, as shown by Debye, that when we put

$$\tau = n - m \tag{280}$$

$$x_{nm} = 2\int_a^b x \frac{m\omega}{p(x)} \cos\left(2\pi\tau \int_a^x \frac{\partial p}{\partial J}\,dx\right) dx .$$

Now we have,

$$\frac{\partial p}{\partial J} = \frac{\partial p}{\partial E} \Big/ \frac{\partial J}{\partial E} = \omega \cdot \frac{m}{p(x)} = \omega/\dot{x} \text{ , and}$$

$$\int_a^x \frac{\partial p}{\partial J}\,dx = \omega t ;$$

therefore

$$x_{nm} = 2\int_0^{1/2\omega} x(t)\,\omega \cos(2\pi\tau\omega t)\,dt = \omega \int_0^{1/\omega} x(t) \cos(2\pi\tau\omega t)\,dt$$

Decomposing the classical motion into a Fourier expansion such that for $t = 0$, $x = a$, we have

$$x = \sum_{\tau=0}^{\infty} a_\tau \cos 2\pi\tau\omega t$$

and $$a_\tau = 2\omega \int_0^{1/\omega} x(t) \cos(2\pi\tau\omega t)\,dt .$$

We will now briefly the relation

$$x_{nm} = \frac{1}{2} a_\tau = \frac{1}{2} a_{n-m} \qquad (281)$$

in the limiting case of large quantum numbers. The factor $\frac{1}{2}$ is correct since the sum

$$x_{n,n+\tau} e^{2\pi i \nu_{n,n+\tau} t} + x_{n,n-\tau} e^{2\pi i \nu_{n,n-\tau} t}$$

transforms exactly to $a_\tau \cos 2\pi\tau\omega t$. We can equally well calculate the momentum matrix instead of the coordinate matrix. By these results we bring out the correspondence with the original form of Bohr's Correspondence Principle.

By connecting together many eigenfunctions into a group we can readily build a packet in the region of large quantum numbers which executes a complete motion in the neighbourhood of the classical orbit. It represents a state according to which there exists approximately the path of a particle. If the packet embraces the state from $n-k$ to $n+k$ the time t which the packet takes to pass by a point has the inaccuracy Δt given by

$$\omega \Delta t \sim 1/k$$

since $\Delta E = \frac{\partial E}{\partial J} \Delta J = \omega k \hbar$, and

$$\Delta E \Delta t \sim h ; \qquad (282)$$

on the other hand, when $\omega t + \delta_0 = w$ is introduced as the angle variable

$$\Delta J \Delta w \sim h. \qquad (282')$$

It is here assumed that the wave packet encloses a large number of states since the phase would otherwise lose all its meaning. It is to be further mentioned that for systems of the considered variety the Δ states are to be

defined not as w but as $e^{i\underline{\underline{w}}}$ (function of p and q) as also the operator J. Here $\underline{\underline{J}}$ is hermitian and $e^{i\underline{\underline{w}}}$ unitary. The two operators satisfy the hermitian exchange relations

$$\underline{\underline{J}}\, e^{i\underline{\underline{w}}} - e^{i\underline{\underline{w}}}\,\underline{\underline{J}} = e^{i\underline{\underline{w}}}\, h \text{ , or } \underline{\underline{J}}\, e^{i\underline{\underline{w}}} = e^{i\underline{\underline{w}}}(\underline{\underline{J}} + h) \qquad (283,a)$$

whereforom by left multiplicatcion with $e^{-i\underline{\underline{w}}}$ as well as right multiplication with $e^{-i\underline{\underline{w}}}$ it follows that

$$e^{-i\underline{\underline{w}}}\,\underline{\underline{J}} - \underline{\underline{J}}\, e^{-i\underline{\underline{w}}} = e^{-i\underline{\underline{w}}}\, h \text{ , or } \underline{\underline{J}}\, e^{-i\underline{\underline{w}}} = e^{-i\underline{\underline{w}}}(\underline{\underline{J}} - h) \qquad (283,b)$$

We shall however not employ these operators for any purpose.

It is essential that the Knowledge of the phase of motion of the particle and of any one of the stationary states should be mutually exclusive. The Umlaufphase (orbit) of the particle does not exist for a single stationary state since every experiment to determine this puts the system into another stationary state. Since further the similarity of the time variation of the density of a wave group to several stationary states with a classical orbit is possible only in the limiting case of large quantum numbers, it follows readily that a wave packet occupies as a consequence of the uncertainty relation at least the surface area h in phasespace, while the classical path with the energy E_n of the nth stationary state encloses the area nh. Only when n is large, is this large area large compared to h, and only then is it possible to have an actual density packet moving.

of a long interval of time. For this it is essential that the frequency

$$\frac{E_{n+\tau} - E_{n+\sigma}}{h}$$

appearing in the density of the packet, with $-k \leqq \tau \leqq +k$, $-k \leqq \sigma \leqq +k$, should not in general be exactly the multiple $(\tau-\sigma)\omega$ of a fundamental frequency as would be the case for a classical periodic orbit, since the classical frequency ω depends in general on the value of the phase integral. We can write approximately

$$\frac{1}{h}\left(E_{n+\tau} - E_n\right) = \tau\omega + \frac{1}{2} h \frac{\partial \omega}{\partial J} \tau^2$$

$$\frac{1}{h}\left(E_{n+\tau} - E_{n+\sigma}\right) = (\tau-\sigma)\omega + \frac{1}{2} h \frac{\partial \omega}{\partial J}\left(\tau^2 - \sigma^2\right).$$

As Darwin has shown this has the consequence that there appears further an uncertainty $kh \frac{\partial \omega}{\partial J}$ besides the uncertainty $1/k$ of the phase. After the time

$$\Delta t \sim \frac{1}{kh\, \partial\omega/\partial J} \qquad (284)$$

the packet is completely mixed up over the total boundary of the orbit and the phase is completely lost. The number N of circuits after which this happens is given by

$$N = \omega \Delta t \sim \frac{\omega}{kh\, \partial\omega/\partial J} \qquad (284')$$

Only for special systems as for eg. the linear harmonic oscillator or the motion of an electron in a plane under the action of a homogeneous

magnetic field perpendicular to the motion, where the frequency ω is rigoro
independent of the initial conditions, does the wave packet keeps permanent
together. In the first case Schrodinger, and in the second Kennard & Darwin
given rigorous solutions for wave groups of these specified conditions

(See next page)

To conclude it is to remarked that while the old quantum theory arrives at conclusions only in the special case of multiply periodic systems, the eigen-value problem of wave mechanics always possesses a solution. Also in the general case it is possible, as we have seen, to construct wave packets which move along the classical orbits. In course of time however there is always a diffusion of the wave-packet, and hence the fact is that in the gross only discrete frequencies appear and thus cannot be immediately connected with the simple periodic properties of classical orbits in long time-intervals. This last behaviour is well-known for eg. the three-body problem is very complicated for long intervals of time, and it is an advance of wave-mechanics that this problem is of no significance so far as its application to atomic systems is considered.

§13. Hamilton-function with transformation groups. Momentum and spin:

When the Hamiltonian of a/an is invariant for a certain group of transformations, it follows that corresponding to one solution $u_n(q)$ of the wave-equation, one obtains by the transformations of the group another new solution.

If $\underline{\underline{I}}$ be a transformation of the group, $\underline{\underline{H}}$ the Hamilton-operator, f an arbitrary function, $u(q)$ a solution of the equation

$$\underline{\underline{H}}\, u(q) = E\, u(q)$$

it follows from the validity of

$$\underline{\underline{I}}\,(\underline{\underline{H}} f) = \underline{\underline{H}}\,(\underline{\underline{I}} f)$$

for all f, that also

$$v(q) = T u(q)$$

satisfies the equation

$$\underline{\underline{H}}\, v(q) = E\, v(q)$$

[Putting $f = u$, $v = \underline{\underline{I}} f = \underline{\underline{I}} u$

$\underline{\underline{I}}(Eu) = E\,\underline{\underline{I}} u$

becomes an identity]

If to the corresponding eigen-value there belong only a finite number of eigen-functions, say h (h-fold degeneracy), there is a basis $u_1 \ldots u_h$ of functions in this h-dimensional space belonging to E so that each solution $v(q)$ of the equation

$$\underline{\underline{H}}\, v = E v$$

can be represented in the form

$$v = \sum_K c_K u_K$$

The transformations $\underline{\underline{I}}$ of the group when applied to $u_1, u_2 \ldots u_h$ accordingly transform this vector space linearly in such a manner that the two different successive transformations $\underline{\underline{I}}$ correspond to two successive corresponding give rise

linear manifolds. In order to bring about consonance with the matrix rule of multiplication, it is thereby useful to introduce the following assumption. When the variables q of the function $u(q)$ are subjected to the transformation $\underline{\underline{T}}$ defined by the transition to new variables $q_\rho' = f_\rho(q_1 \cdots q_f)$ we can make this transformations of the variables q correspond to an operator $\underline{\underline{T}}$ which transforms the function $u(q_1 \cdots q_f)$ to $u'(q_1 \cdots q_f)$:

$$\underline{\underline{T}}\, u \equiv u'$$

wherefrom $u'(q_1', \cdots q_f') = u(q_1, q_2 \cdots q_f)$, ie

$$u'(\underline{\underline{T}} q) = u(q)$$

or $$u'(q) = u(\underline{\underline{T}}^{-1} q)$$

Only in this case is there correspondence between the combination of two operators in the order first $\underline{\underline{T}}_2$, then $\underline{\underline{T}}_1$ and the same order of the transformations of the variables. In fact

$$\underline{\underline{T}}_2\, u(q) = u'(q) = u(\underline{\underline{T}}_2^{-1} q)$$

and substituting $\underline{\underline{T}}^{-1} q$ for q, this gives correctly

$$(\underline{\underline{T}}_1\ \underline{\underline{T}}_2)\, u = \underline{\underline{T}}_1\, u'(q) = u'(\underline{\underline{T}}_1^{-1} q) = u(\underline{\underline{T}}_2^{-1} \underline{\underline{T}}_1^{-1} q)$$

and $$(\underline{\underline{T}}_1\ \underline{\underline{T}}_2)\, u = u\left((\underline{\underline{T}}_1\, \underline{\underline{T}}_2)^{-1} q\right)$$

[The right order for $(\underline{\underline{T}}_1 \underline{\underline{T}}_2)^{-1}$ is $\underline{\underline{T}}_2^{-1}\, \underline{\underline{T}}_1^{-1}$ and this is satisfied]

In the matrix method of writing we put

$$(\underline{\underline{T}}\, u_l) = \sum_{k=1}^{h} u_k\, c_{kl} \qquad (285)$$

Then we have

$$c_{kl}\left(\underline{\underline{T}}_1\,\underline{\underline{T}}_2\right) = \sum_m c_{km}\left(\underline{\underline{T}}_1\right) c_{ml}\left(\underline{\underline{T}}_2\right) \qquad (286)$$

[$\left(\underline{\underline{T}}_1\,\underline{\underline{T}}_2\right) u_l = \sum_k u_k\, c_{kl}\left(\underline{\underline{T}}_1\,\underline{\underline{T}}_2\right)$

$\left(\underline{\underline{T}}_1\,\underline{\underline{T}}_2\right) u_l = \underline{\underline{T}}_1 \sum_m u_m\, c_{ml}\left(\underline{\underline{T}}_2\right) = \sum_k \sum_m u_k\, c_{km}\left(\underline{\underline{T}}_1\right) c_{ml}\left(\underline{\underline{T}}_2\right)$

ie $c_{kl}\left(\underline{\underline{T}}_1\,\underline{\underline{T}}_2\right) = \sum_m c_{km}\left(\underline{\underline{T}}_1\right) c_{ml}\left(\underline{\underline{T}}_2\right)$]

or in the matrix-method of writing

$$\underline{\underline{c}}\left(\underline{\underline{T}}_1\,\underline{\underline{T}}_2\right) = \underline{\underline{c}}\left(\underline{\underline{T}}_1\right)\underline{\underline{c}}\left(\underline{\underline{T}}_2\right) \qquad (286')$$

We then say that the corresponding linear manifolds form a <u>representation</u> of the group. Naturally, <u>different</u> transformations of the group can correspond to the same linear manifold in the representation. If the determinant of the new variables $q_\rho' = f_\rho(q_1 \cdots q_f)$ which are defined by $\underline{\underline{T}}$ with respect to the old variables q_ρ has the value 1, and besides q_ρ' as well as q_ρ are real then it follows with

$$\underline{\underline{T}}\, v(q_1 \cdots q_f) = v\left(f_1(q), f_2(q), \ldots f_f(q)\right)$$

[$d(qq')\ \underline{\underline{T}} v \equiv v'(q)$, and because the determinant of the transformation $q' = f(q)$ is unity, we have $v'(q) = v(q')$]

that $$\int v_k^* v_l\, dq = \int \left(\underline{\underline{T}}\, v_k\right)^* \left(\underline{\underline{T}}\, v_l\right) dq$$

[The right hand side $= \int v_k^*(q')\, v_l(q')\, dq'$, from the above

$= \int v_k^* v_l\, dq$, since the Jacobian is unity]

In this case the matrices $\underline{\underline{C}}(\underline{\underline{T}})$ are unitary for all $\underline{\underline{T}}$, and hence one calls the representation also unitary. In this case a normal orthogonal system is transformed into a normal orthogonal system.

Of essential significance is the notion of reduction of a representation. A representation is said to be reducible when an invariant sub-space of dimensions less than the original representation space always exists, ie by one can choose a basis of linearly independent functions $u_1 \dots u_g$ $(g < h)$ forming only a part of the total basis $u_1 \dots u_h$ such that the transformations T transform inside the g-basis alone. The total matrix $\underline{\underline{C}}(\underline{\underline{T}})$ has by this choice of basis the form

$$\underline{\underline{C}} = \begin{pmatrix} \underline{\underline{a}} & \underline{\underline{r}} \\ 0 & \underline{\underline{b}} \end{pmatrix} \qquad (287)$$

where $\underline{\underline{a}}$ is g-dimensional, and $\underline{\underline{b}}$ is $(h-g)$-dimensional

[This follows from the fact the product of two matrices of the form (287) will be another matrix of the same form]

If there be no such genuine invariant sub-space the representation is said to be irreducible. Change of basis signifies a transformation $\underline{\underline{C}}' = \underline{\underline{S}}\,\underline{\underline{C}}\,\underline{\underline{S}}^{-1}$

[If $\underline{\underline{C}}'(\underline{\underline{T}}_1 \underline{\underline{T}}_2) = \underline{\underline{C}}'(\underline{\underline{T}}_1)\,\underline{\underline{C}}''(\underline{\underline{T}}_2)$ holds when (286') is true if $\underline{\underline{C}}' = \underline{\underline{S}}\,\underline{\underline{C}}\,\underline{\underline{S}}^{-1}$]

of the representation matrix, and two representations which can be distinguished only in this manner are said to be equivalent. When $\underline{\underline{C}}$ is an unitary matrix it follows from the form (287) readily that by a change of basis even $\underline{\underline{r}}$ can be

made equal to zero ie the representation splits up.

$$\left[\underline{\underline{c}}\,\tilde{\underline{\underline{c}}} = \begin{pmatrix} \underline{\underline{a}} & \underline{\underline{r}} \\ \underline{\underline{0}} & \underline{\underline{b}} \end{pmatrix} \begin{pmatrix} \tilde{\underline{\underline{a}}} & \underline{\underline{0}} \\ \tilde{\underline{\underline{r}}} & \tilde{\underline{\underline{b}}} \end{pmatrix} = \begin{pmatrix} a\tilde{a} + r\tilde{r} & r\tilde{b} \\ b\tilde{r} & b\tilde{b} \end{pmatrix} \right.$$ and since this is equal to $\underline{\underline{1}}$

the non-diagonal elements are zero ie $\underline{\underline{r}} = 0$; if $\underline{\underline{b}} = 0$, $\underline{\underline{c}} \equiv \underline{\underline{a}}$ and no question of reducibility arises. Thus if in $\underline{\underline{c}}$, we had $\underline{\underline{r}} = 0$, $\underline{\underline{c}}\,\tilde{\underline{\underline{c}}} = 1$, which shows that by a change of basis $\underline{\underline{r}}$ can be made equal to 0 in $\underline{\underline{c}}$ $\left.\right]$

For a finite group it can be proved that all representations of an unitary representation are equivalent, and that accordingly every reducible representation also splits up. For continuous groups this does not always hold but only for a determinate class of these groups the so-called semi-simple groups. The rotation group is one such, as also the group of all linear transformations with the determinant 1, where, however, the last restriction is essential. Since one usually deals only with unitary representations in quantum-mechanics, we shall not enter into the complications of the general case.

Accordingly every representation (D) of a group splits up into irreducible representations according to

$$(D) = (D_1) + (D_2) + \cdots,$$

and it can be easily shown that the splitting up is unique. The degeneracy belonging to the concerned eigenvalue of the energy and which corresponds to the order of the irreducible representation cannot be removed by a continuous change of the Hamiltonian so long as it is invariant with

respect to the group (in contrast to the "accidental" degeneracy which corresponds to the higher order of a reducible representation). If however the Hamiltonian operator be so changed as to be invariant only for a sub-group of the original group, the representation is in general reducible with respect to these smaller groups. The change in the choice of the basis which brings about the splitting up of the representation, and which can also be denoted as the reduction of the original representation with respect to the sub-group, corresponds (in general) to the splitting up of the original eigenvalues of the energy as soon as a perturbation function is introduced which again is invariant for this sub-group.

From two representations (D_1) and (D_2) of orders h_1 and h_2 can, in general, a product representation $(D_1 \times D_2)$ of order $h_1 \cdot h_2$ can be constructed in the following manner. From the basis u_k $(k = 1, 2 \ldots h_1)$ of (D_1) and v_l $(l = 1, \ldots h_2)$ of (D_2) construct the $h_1 \cdot h_2$ products $u_k v_l$. If the u_k give rise to a linear manifold $D_1(T)$ and a v_l a $D_2(T)$, then $u_k v_l$ equally give rise to a linear manifold which is defined as $(D_1 \times D_2)$. In particular (D_1) can be equal to (D_2). Naturally $(D_1 \times D_2)$ is in general reducible even when (D_1) and (D_2) are irreducible. By the change of choice of basis of the $h_1 h_2$-dimensional space, $(D_1 \times D_2)$ can also be split up, whereby the irreducible parts of (D_1) and (D_2) might be different.

This product-formation of representations appears readily by the coupling of independent systems.

In the case of continuous groups, the special infinitesimal transformations which lie near the identity are of interest. These form a linear manifold, a vector-space of as many dimensions as the number of independent parameters contained in the group (for the group of rotations of three-dimensional space we have accordingly a three-dimensional vector space). In fact it follows from $\underline{\underline{I}}(0, 0, \cdots 0) = \underline{\underline{1}}$, that

$$\underline{\underline{I}}(\epsilon_1, \epsilon_2, \cdots \epsilon_r) = \underline{\underline{1}} + \epsilon_1 \underline{\underline{\omega}}_1 + \epsilon_2 \underline{\underline{\omega}}_2 + \cdots + \epsilon_r \underline{\underline{\omega}}_r ,$$

the dependence of $\underline{\underline{I}}$ on the ϵ's being continuous. The $\underline{\underline{\omega}}_1, \underline{\underline{\omega}}_2, \cdots \underline{\underline{\omega}}_r$ operate just like the $\underline{\underline{I}}$ operators on the variables q of the eigen-functions. The fact that the concerned transformation generates a group requires that the "bracket-symbol" $[\underline{\underline{\omega}}_p, \underline{\underline{\omega}}_q] = \underline{\underline{\omega}}_p \underline{\underline{\omega}}_q - \underline{\underline{\omega}}_q \underline{\underline{\omega}}_p$, should be further expressible in terms of the $\underline{\underline{\omega}}$, with- and with- coefficients which are characteristic for the concerned group

$$[\underline{\underline{\omega}}_p, \underline{\underline{\omega}}_q] = \sum_{s=1}^{r} c_{pq,s} \underline{\underline{\omega}}_s \qquad (288)$$

These coefficients must satisfy certain relations which arise from the identities

$$[[\underline{\underline{\omega}}_p, \underline{\underline{\omega}}_q], \underline{\underline{\omega}}_r] + [[\underline{\underline{\omega}}_q, \underline{\underline{\omega}}_r], \underline{\underline{\omega}}_p] + [[\underline{\underline{\omega}}_r, \underline{\underline{\omega}}_p], \underline{\underline{\omega}}_q] = 0.$$

In view of the assumption made above of the relation between the operators

acting on the eigen-functions, and the transformations of the variables, both these satisfy the same exchange relations, and it is usual useful not to distinguish between them in the notation. The fact that the Hamilton operator is invariant for the group is expressed thus:

$$\underline{\underline{\omega}}_p \underline{\underline{H}} - \underline{\underline{H}} \underline{\underline{\omega}}_p = 0$$

$\left[\underline{\underline{I}} (\underline{\underline{H}} f) = \underline{\underline{H}} (\underline{\underline{I}} f) \text{ gives this relation} \right]$

as is also the case for an operator $\underline{\underline{I}}$ of the finite transformation. This is equivalent to saying that the matrices $\underline{\underline{\omega}}_p$ are constants of the time ie are integrals of the equations of motion. When $\underline{\underline{I}}$ is unitary the $\underline{\underline{\omega}}_p$ are hermitian except for a factor i. For every representation of the group there belongs a system of matrices for the $\underline{\underline{\omega}}_K$ which satisfy the relations (288).

For eg. for the group of translations by which the coordinates $x_k^{(a)}$ $(k = 1, 2, 3)$ are displaced by A_K, ie

$$x'^{(a)}_k = x_k^{(a)} + A_K \qquad (A_1, A_2, A_3 \text{ continuous parameters})$$

$\underline{\underline{\omega}}_K = \sum_a \frac{\partial}{\partial x_K^{(a)}}$. This corresponds except for the factor $\hbar/i$ with the total momentum of the system. In fact, the invariance of the Hamilton function for this group is equivalent to the fact that the potential energy depends

only on the relative coordinates of the particles.

We now proceed to consider the simultaneous rotation of the space-coordinates for all the particles of the system. We can here adopt two different methods. Either one places himself in the infinitesimal standpoint, determines the form of the operators $\underline{\omega}_k$ belonging to the infinitesimal rotations, and the representation matrices in a purely algebraic way on the basis of the exchange relations of the operators. Or one finds the representations belonging to finite rotations in the analytical way. The two methods supplement each other. We start here with the first method.

As the three independent rotations of the three dimensional space we choose the rotations about the coordinate axes

$$\delta x_1 = 0\,, \quad \delta x_2 = -\epsilon_1 x_3\,, \quad \delta x_3 = +\epsilon_1 x_2 \tag{289}$$

the two remaining rotations being obtained by cyclic interchange. On the basis of elementary kinematical considerations (transition of finite to infinitesimal rotations) we obtain the V-R characteristic for infinitesimal rotations

$$\underline{\underline{\omega}}_1 \underline{\underline{\omega}}_2 - \underline{\underline{\omega}}_2 \underline{\underline{\omega}}_1 = \underline{\underline{\omega}}_3 \tag{290}$$

if the operators or the corresponding linear manifolds be so defined that for eg the operator $\underline{\underline{1}} + \epsilon_1 \underline{\underline{\omega}}_1$ belongs to the transformation (289). This relation must also be satisfied for <u>all</u> representations of the rotation group. Since we

shall consider later also reflections of the space-coordinates, we shall assume that the $\underline{\underline{\omega}}$'s behave like a skew-symmetric tensor for these reflections / rotations, and not like a vector. Writing accordingly $\underline{\underline{\omega}}_{23}, \underline{\underline{\omega}}_{31}, \underline{\underline{\omega}}_{12}$ instead of $\underline{\underline{\omega}}_1, \underline{\underline{\omega}}_2, \underline{\underline{\omega}}_3$ (with $\underline{\underline{\omega}}_{ki} = -\underline{\underline{\omega}}_{ik}$) we can write (289) in the form

$$\underline{\underline{\omega}}_{ik}\,\underline{\underline{\omega}}_{lm} - \underline{\underline{\omega}}_{lm}\,\underline{\underline{\omega}}_{ik} = \delta_{kl}\,\underline{\underline{\omega}}_{im} + \delta_{im}\,\underline{\underline{\omega}}_{kl} - \delta_{il}\,\underline{\underline{\omega}}_{km} - \delta_{km}\,\underline{\underline{\omega}}_{il} \qquad (290')$$

($\delta_{ik} = 0$, for $i \neq k$, and $= 1$ for $i = k$). This form of the exchange relation ~~is also verified~~ for infinitesimal rotations is also correct in an n-dimensional space, as we shall make use of it later for the treatment of the Lorentz group.

According to ~~previous~~ our earlier assumption an infinitesimal rotation (289) belonging to the operator $\underline{1} + \epsilon\,\underline{\underline{\omega}}_1$ (or $\underline{1} + \epsilon\,\underline{\underline{\omega}}_{23}$) transforms in the case of a single particle

$$u(x_1, x_2, x_3) \text{ to } u(x_1, x_2 + \epsilon x_3, x_3 - \epsilon x_2);$$

$$\left[\; u'(q) = u(\underline{\underline{I}}^{-1} q)\right]$$

accordingly $$\underline{\underline{\omega}}_1 u = -\left(x_2 \frac{\partial u}{\partial x_3} - x_3 \frac{\partial u}{\partial x_2}\right)$$

$$\left[\; u(x_1, x_2 + \epsilon x_3, x_3 - \epsilon x_2) = u(x_1, x_2, x_3) + \left(\epsilon x_3 \frac{\partial}{\partial x_2} - \epsilon x_2 \frac{\partial}{\partial x_3}\right) u + \cdots \right.$$

$$\left. = (1 + \epsilon\,\underline{\underline{\omega}}_1)\, u \right]$$

For many particles, the coordinates of all the particles must be subject to the

same rotation, and we have

$$\underline{\underline{\omega}}_1 u = -\sum_r \left(x_2^{(r)} \frac{\partial u}{\partial x_3^{(r)}} - x_3^{(r)} \frac{\partial u}{\partial x_2^{(r)}} \right)$$

the summation being over all the particles present. Since the linear momentum $\underline{\underline{p}}_k^{(r)}$ is represented by the operator $\frac{\hbar}{i} \frac{\partial}{\partial x_k^{(r)}}$, $\underline{\underline{\omega}}$ depends in the simplest manner on the total angular momentum

$$\underline{\underline{P}}_1 = \sum_r \left(\underline{\underline{x}}_2^{(r)} \underline{\underline{p}}_3^{(r)} - \underline{\underline{x}}_3^{(r)} \underline{\underline{p}}_2^{(r)} \right) = \frac{\hbar}{i} \sum_r \left(x_2^{(r)} \frac{\partial}{\partial x_3^{(r)}} - x_3^{(r)} \frac{\partial}{\partial x_2^{(r)}} \right) \qquad (291)$$

according to

$$\underline{\underline{\omega}}_K = -\frac{i}{\hbar} \underline{\underline{P}}_K \qquad (292)$$

whereby it is again confirmed that ω differs from a hermitian operator by the factor i. From the exchange relations (103) for the $\underline{\underline{p}}_K$ and $\underline{\underline{q}}_K$ it follows that

$$\underline{\underline{P}}_1 \underline{\underline{P}}_2 - \underline{\underline{P}}_2 \underline{\underline{P}}_1 = -\frac{\hbar}{i} \underline{\underline{P}}_3 \qquad (293)$$

It is however important to notice that the existence of the integrals of the three components of angular momentum which coincides, except for a purely imaginary factor, with the operators $\underline{\underline{\omega}}$ belonging to infinitesimal rotations can be deduced independently of the exchange relations (103) because the exchange relations of the $\underline{\underline{\omega}}$ arise directly from the kinematics of the rotation group. Further are valid also the V-R,

$$\left[\underline{\underline{\omega}}_K , \underline{\underline{C}} \right] = 0 , \quad \text{or} \quad \left[\underline{\underline{P}}_K , \underline{\underline{C}} \right] = 0 \qquad (294)$$

for every scalar $\underline{\underline{C}}$, and

$$[\underline{\underline{\omega}}_1 , \underline{\underline{A}}_2] = -[\underline{\underline{\omega}}_2 \underline{\underline{A}}_1] = \underline{\underline{A}}_3 \qquad (295)$$

and, $$[\underline{\underline{P}}_1 , \underline{\underline{A}}_2] = -[\underline{\underline{P}}_2 , \underline{\underline{A}}_1] = -\frac{\hbar}{i}\underline{\underline{A}}_3 \qquad (295')$$

for the components of every vector operator $\vec{\underline{\underline{A}}}$. Here it is assumed that $\underline{\underline{C}}$ and $\vec{\underline{\underline{A}}}$ are functions of $\underline{\underline{P}}_k$, $\underline{\underline{q}}_k$ alone while no vectors which are ordinary numbers are employed. These V-R can also be deduced from the following relations valid for finite rotations

$$\underline{\underline{T}}\,\underline{\underline{C}} = \underline{\underline{C}}\,\underline{\underline{T}} \quad \text{or} \quad \underline{\underline{T}}\,\underline{\underline{C}}\,\underline{\underline{T}}^{-1} = \underline{\underline{C}} \qquad (296)$$

and $$\underline{\underline{T}}\,\underline{\underline{A}}'_k = \underline{\underline{A}}_k \underline{\underline{T}} \quad \text{or} \quad \underline{\underline{A}}'_k = \underline{\underline{T}}^{-1}\underline{\underline{A}}_k\underline{\underline{T}} \qquad (297)$$

by specialising for the case of infinitesimal rotations. The first relation states the invariance of $\underline{\underline{C}}$ (as for the Hamilton operator), the second the covariance of $\vec{\underline{\underline{A}}}$ for rotations. The existence of such a unitary $\underline{\underline{T}}$ follows easily from the fact that the totality of the $\underline{\underline{A}}'_k$ ~~satisfy~~ possess the same eigen-values as $\underline{\underline{A}}_k$, and satisfy the same V-R. On the basis of (291) and the fundamental V-R (103) it can be verified that (296) and (297) also follows from them. In particular these relations are valid for $\underline{\underline{A}}_k = \underline{\underline{p}}_k^{(r)}$ or $\underline{\underline{A}}_k = \underline{\underline{q}}_k^{(r)}$ and also (294) for $\underline{\underline{C}} = \underline{\underline{P}}^2 = \underline{\underline{P}}_1^2 + \underline{\underline{P}}_2^2 + \underline{\underline{P}}_3^2$ as ~~also~~ follows again directly from (293).

$$\underline{\underline{P}}^2\,\underline{\underline{P}}_k - \underline{\underline{P}}_k\,\underline{\underline{P}}^2 = 0. \qquad (298)$$

This makes it possible to assert that $\underline{\underline{P}}^2$ and a component $\underline{\underline{P}}_k$ can be

$$\left.\begin{aligned}
(\underline{\underline{A_1}} + i\,\underline{\underline{A_2}})_{j,m+1;\,j,m} &= A_{j,j}\sqrt{(j+m+1)(j-m)} \\
(\underline{\underline{A_1}} - i\,\underline{\underline{A_2}})_{j,m-1;\,j,m} &= A_{j,j}\sqrt{(j+m)(j-m+1)} \\
(A_3)_{j,m;\,j,m} &= A_{jj}\cdot m
\end{aligned}\right\} \qquad (301'b)$$

$$\left.\begin{aligned}
(\underline{\underline{A_1}} + i\,\underline{\underline{A_2}})_{j-1,m+1;\,j,m} &= A_{j-1,j}\sqrt{(j-m)(j-m-1)} \\
(\underline{\underline{A_1}} - i\,\underline{\underline{A_2}})_{j-1,m-1;\,j,m} &= -A_{j-1,j}\sqrt{(j+m)(j+m-1)} \\
(A_3)_{j-1,m;\,j,m} &= A_{j-1,j}\sqrt{(j+m)(j-m)}
\end{aligned}\right\} \qquad (301'c)$$

For all other pairs of values of j,m in initial and final states the matrix-elements vanish. The selection- and intensity rules for j and m are contained in the above relations.

We have to make a further remark about the combination of two systems with the angular momenta j_1 and j_2. Let $\underline{\underline{P}}_3^{(1)}$ and $\underline{\underline{P}}_3^{(2)}$ be both brought to the diagonal form, and let their corresponding eigenvalues be m_1 and m_2 running from $-j_1$ to $+j_1$ and $-j_2$ to $+j_2$ respectively. We now form the total momentum $\underline{P}_r = \underline{P}_r^{(1)} + \underline{P}_r^{(2)}$ and its square $\underline{\underline{P}}^2 = \sum_{r=1}^{3} \underline{\underline{P}}_r^2$. $\underline{\underline{P}}_3$ is in diagonal form and every one of its eigen-values

$$m = m_1 + m_2$$

appears as often as it can be obtained by addition of numbers in the intervals $(-j_1, +j_1)$ and $(-j_2, +j_2)$. Let us put $j_1 \geq j_2$, we find this number $Z(m)$ as follows:

for $j_1 - j_2 \leqq m \leqq j_1 + j_2$ $\qquad Z(m) = j_1 + j_2 - m + 1$

$-(j_1 - j_2) \leqq m \leqq j_1 - j_2$ $\qquad Z(m) = 2j_2 + 1$

$-(j_1 + j_2) \leqq m \leqq -(j_1 - j_2)$ $\qquad Z(m) = j_1 + j_2 + m$

when we bring each $\underline{P}^2$ separately to diagonal form for each m, instead of m_1 and m_2, we obtain a series of states with different j in such a way that for each j, m runs from $-j$ to $+j$. If the value j appears $N(j)$ times, we obtain the total number of states $Z(m)$ for determined m as

$$Z(m) = \sum_{j \geqq m} N(j)$$

This is correct for $m \geqq 0$ to which alone we can confine ourselves since the case $m \leqq 0$ does not lead to anything new. It follows further

$$N(j) = Z(j) - Z(j+1)$$

This means that in our case all values of j increasing by unity appear in, and only in the interval

$$|j_1 - j_2| \leqq j \leqq j_1 + j_2 \qquad (302)$$

And that too exactly once which corresponds with to the "vector-model" of the old quantum theory. For representations of finite rotations it follows from the definition of product of representations introduced before that

$$(D_{j_1}) \times (D_{j_2}) = \sum_{j = |j_1 - j_2|}^{j_1 + j_2} (D_j) \qquad (302')$$

So far the cases of half integral and integral j are completely on the same

footing. In §6, however, we have proved that for a particle in a central field where the angular-momentum quantum number denoted by l (instead of j) is always integral. From (302) it follows that the same is true for many particles, and this is not altered by the insertion of arbitrary interaction forces between the particles (because of their continuity). On account of the spin important generalisations are necessary in order that the V-R (293) of angular momentum matrices as well as the V-R (294) and (295) might be consistent with half-integral j and m. First of all it might be mentioned that the integral nature of these quantum numbers follows from the definition (291) of the angular momentum in together with the V-R for coordinates and momenta (Le Born-Jordan p. 164). We have therefore to generalise the definition (291) further.

We will now give the irreducible representations of finite groups (second method) which corresponds to the different integral and half-integral values of j. For this it is useful to consider, instead of the group of rotations in three dimensional space, first of all the group U_2 of unitary transformations with determinant 1 of two complex variables ξ_1, ξ_2. These have the form

$$\left.\begin{aligned} \xi_1' &= \xi_1 \alpha - \xi_2 \beta^* \\ \xi_2' &= \xi_2 \beta + \xi_2 \alpha^* \end{aligned}\right\} \qquad (303)$$

with $\alpha\alpha^* + \beta\beta^* = 1$ (304)

The corresponding transformation of the a_1, a_2 which leaves the bilinear form

$$a_1 \xi_1 + a_2 \xi_2$$

invariant is

$$\left.\begin{aligned} a_1' &= \alpha a_1 + \beta a_2 \\ a_2' &= -\beta^* a_1 + \alpha^* a_2 \end{aligned}\right\} \qquad (303')$$

According to (303) the $(v+1)$ products of powers

$$\xi_1^v, \xi_1^{v-1}\xi_2, \cdots, \xi_2^v$$

transform linearly into each other. This yields a representation of the considered group of order $v+1$. It is besides irreducible. If we introduce a new basis of vectors given by

$$\Xi_r = \frac{\xi_1^{v-r}\xi_2^r}{\sqrt{r!(v-r)!}} \qquad (r = 0, 1, \cdots v) \qquad (305)$$

we obtain even an unitary representation since $(\xi_1\xi_1^* + \xi_2\xi_2^*)^v$ just like $(\xi_1\xi_1^* + \xi_2\xi_2^*)$ must be invariant, and this corresponds with Coincides

$\sum_r \Xi_r \Xi_r^*$. [The invariance of this means "length-invariance" ie representation is unitary. The question of splitting up of the representation does not arise although it is unitary since the representation is irreducible]. Putting $v = 2j$ and $r = j - m$ we can relate the present results to the previous notation.

We thus obtain a representation D_j of order $2j+1$ of the group of unitary transformations of determinant 1. D_0 is the identical representation, $D_{1/2}$ is the original transformation itself.

The connection with the group of rotations of three dimensional space

results when we consider D_1. For $j = 1$, $v = 2$ we transform c_0, c_1, c_2 so that

$$\tfrac{1}{2} c_0 \xi_1^2 + c_1 \xi_1 \xi_2 + \tfrac{1}{2} c_2 \xi_2^2$$

remains invariant. Since the determinant of the transformation is unity, the determinant

$$\begin{vmatrix} c_1 & c_0 \\ c_2 & c_1 \end{vmatrix} = c_1^2 - c_0 c_2$$

remains invariant. Putting

$$x + iy = c_2 \; ; \; x - iy = -c_0 \; , \; z = c_1 \qquad (306)$$

we have, $x^2 + y^2 + z^2 = |x+iy||x-iy| + z^2 = c_1^2 - c_0 c_2$,

hence the manifold D_1 denotes ordinary rotations in (x, y, z)-space. It can be easily shown that the x, y, z transform like

$$a_1 a_2^* + a_2 a_1^* \; ; \; i(a_1 a_2^* - a_2 a_1^*) \; , \; a_1 a_1^* - a_2 a_2^*$$

when a_1, a_2 transform as in (303'). Since these are real numbers we are dealing here with real rotations. To a rotation with the Eulerian angles ϑ, φ, ψ correspond the transformation-coefficients in (303) & (303') according to

$$\alpha = \cos\frac{\vartheta}{2} e^{-\frac{i}{2}(\varphi+\psi)} \; ; \; \beta = -i \sin\frac{\vartheta}{2} e^{-\frac{i}{2}(\varphi+\psi)} \; , \qquad (307)$$

For $\vartheta = 0$ there results the special case of rotation about the z-axis through the angle $\varphi + \psi$, which would make the matrix diagonal.

[In this case $\beta = 0$, and $\xi_1'^2 = \xi_1^2$; $\xi_1' \xi_2' = \xi_1 \xi_2$, $\xi_2'^2 = \xi_2^2$ ie $C_{KL}(\underline{I}) = \delta_{KL}$]

The identity for 2-face rotations corresponds not only to the identity of the

transformations (303) but also the transformation

$$\xi_1' = -\xi_1 \; ; \; \xi_2' = -\xi_2$$

[In this case also $\xi_1'^2 = \xi_1^2$; $\xi_1'\xi_2' = \xi_1\xi_2$; $\xi_2'^2 = \xi_2^2$]

Therefore the rotations are an abbreviated representation of U_2 and conversely $D_{1/2}$ is a two-valued representation of the rotation group. With the help of (307), and by the consideration of the magnitudes Ξ_ν defined in (305) the general representation matrices of D_j can be calculated as functions of the angles ϑ, φ, ψ (P. Güttinger; Zs. f. Phys. 73, p. 169, 1931). Relative to the sub group of rotations about the z-axis they are readily simplified. For half-integral j we obtain double-valued, and for integral j one-valued representations. The spherical harmonics of the ℓth order transform themselves according to D_ℓ.

We must now remark notice further that the Hamilton-function is always invariant for the reflection

$$x_\kappa' = -x_\kappa \qquad (308)$$

about the centroid of the system. This reflection is commutative with all rotations. Hence every eigenfunction must be simply multiplied by a factor by these reflections (We can also think of an external magnetic field $\mathfrak{H}$ as completely removing the degeneracy governed by the rotation group without altering the invariance of the Hamiltonian for these reflections). Since a double reflection gives the identity, this factor which by definition is given by

$$u(-q_1, \cdots, -q_f) = \epsilon\, u(q_1, \cdots q_f) \qquad (309)$$

can only be equal to ± 1:

$$\epsilon = \pm 1 \qquad (310)$$

we call this factor the reflection-moment or the signature. A term is said to be ~~ad~~ odd or even according as $\epsilon = +1$ or $\epsilon = -1$. For a single particle in a central field it follows from the properties of the spherical harmonics that

$$\epsilon = (-1)^l$$

and hence in general for many particles

$$\epsilon = (-1)^{l_1 + l_2 + \cdots + l_f} \qquad (311)$$

This is valid first of all only for uncoupled particles, but the insertion of coupling forces would not change this on account of their continuity. The matrices of the coordinates of the particles are different from zero when and only when ϵ has different signs in the initial and final states (Laporte's Rule).

With these preliminary notions we can readily set up the generalised wave-equations for particles with spin. Originally one used to consider only the elementary particles (Electrons & protons). We shall however understand by the spin of a particle in general an angular momentum which cannot be traced back to the translational motion of the particles, and whose magnitude (as opposed to its components) is to be considered a fixed number. This standpoint appears necessary since in the present position of quantum theory it is necessary to picture in this way

the spin not merely of the elementary particles but also atomic nuclei. Because it does not appear to be possible to describe the state of a nucleus by eigen-functions containing the position coordinates of the electrons appearing in the nuclei. We can however describe completely the reaction of a nucleus to external forces in so far as it can be considered stationary in an excited state by means of a wave function which contains besides the nuclear coordinates a further spin coordinate as an independent variable.

The description of the spin depends on the following assumptions:

(i) Besides the orbital angular momentum

$$\underline{\underline{l}}_1 = \frac{1}{i}\left(x_1 \frac{\partial}{\partial x_2} - x_2 \frac{\partial}{\partial x_1}\right) \qquad (312)$$

there is a spin moment with the components S_1, S_2, S_3 which can also be related to operators acting on the wave-function. This operator should be commutative with the positional and momentum coordinates of the particles. The angular momenta are measured in units of $\hbar$.

(ii) The infinitesimal rotations

$$\underline{\underline{\omega}}_K = i(\underline{\underline{l}}_K + \underline{\underline{s}}_K) \qquad (313)$$

might be made to correspond to the applications of the operators on the eigen-functions, so that

$$\underline{\underline{P}}_K = \hbar(\underline{\underline{l}}_K + \underline{\underline{s}}_K) \qquad (313')$$

plays the role of the total angular momentum. In fact this total operator is commutative with all rotation-invariant operators and when the

Hamiltonian is rotation-invariant, it is a constant of the time. If the Hamiltonfunction is invariant only for rotations about an axis say the x_3-axis then $\underline{\underline{P}}_3$ is a constant. From these assumptions it follows the V-R (290) for the $\underline{\underline{\omega}}_k$ follow in a purely Kinematic way, and since $\underline{\underline{l}}_k$ are commutative with the $\underline{\underline{S}}_k$, we can deduce the V-R. analogous to (293):

$$\underline{\underline{S}}_1 \underline{\underline{S}}_2 - \underline{\underline{S}}_2 \underline{\underline{S}}_1 = i \underline{\underline{S}}_3 \tag{314}$$

Since we have seen that

$$\underline{\underline{S}}_1^2 + \underline{\underline{S}}_2^2 + \underline{\underline{S}}_3^2$$

is to be considered as a pure number which according to (314) has values $s(s+1)$ (s integral or half-integral):

$$\underline{\underline{S}}_1^2 + \underline{\underline{S}}_2^2 + \underline{\underline{S}}_3^2 = s(s+1) \cdot \underline{\underline{I}} \tag{315}$$

we can introduce in the wave function, besides the particle coordinates x_k, further one of the components S_k, say S_3, such that the wave-function has the form

$$\psi(x, s_3; t) \tag{316}$$

But, as we have seen, S_3 is capable of taking on only the values $-s, -(s-1), \ldots +s$.

Instead of (316) we can also write

$$\psi(x, s_3; t) = \sum_{\mu} c_\mu(s_3)\, \psi_\mu(x,t) \tag{316'}$$

where the $c_\mu(s_3)$ which is independent of x, and t is defined by

$$c_\mu(s_3) = \begin{cases} 1 & \text{for } s_3 = \mu \\ 0 & \text{otherwise} \end{cases} \tag{317}$$

Here $C_\mu(S_3)$ are normalised and orthogonal i.e. we have

$$\sum_{S_3=-S}^{+S} C_\mu^*(S_3)\, C_{\mu'}(S_3) = \begin{cases} 1 & \text{for } \mu = \mu' \\ 0 & \text{for } \mu \neq \mu' \end{cases} \qquad (317')$$

For applications the special choice of $C_\mu(S_3)$ in equation (317) is not essential but only the relation (317') which is invariant for rotations of the axes.

In general $\psi_\mu^* \psi_\mu$ is again the probability in position-spin-space since we have the density in space of position coordinates alone is

$$\rho = \sum_{S_3} \psi^*(x, S_3; t)\, \psi(x, S_3; t) = \sum_\mu \psi_\mu^*(x,t)\, \psi_\mu(x,t) \qquad (318)$$

Its volume integral is time-constant, and accordingly the orthonormal conditions for the ~~stationary~~ eigen-functions belonging to stationary states viz

$$u(x, S_3) = \sum_\mu C_\mu(S_3)\, u_\mu(x)$$

are

$$\sum_{S_3} \int dx\, u_n^*(x, S_3)\, u_m(x, S_3) = \sum_\mu \int dx\, u_{n\mu}^*(x)\, u_{m\mu}(x) = \begin{cases} 1, & \text{for } m = n \\ 0 & \text{for } m \neq n \end{cases} \qquad (318')$$

The components of the current vector will be treated in the Relativistic theory.

As to how the operators $\underline{S}_1$, $\underline{S}_2$, $\underline{S}_3$ act on the wave functions follows immediately from the matrix-representation (301) which here reads

$$\left.\begin{aligned} \left(\underline{S}_1 + i\,\underline{S}_2\right)_{\mu+1,\mu} &= \sqrt{(S-\mu)(S+1+\mu)} \\ \left(\underline{S}_1 - i\,\underline{S}_2\right)_{\mu-1,\mu} &= \sqrt{(S-\mu+1)(S+\mu)} \\ (S_3)_{\mu\mu} &= \mu \end{aligned}\right\} \qquad (319)$$

we have then generally

$$(\underline{\underline{S}}_K)\,\psi_\mu(x,t) = \sum_{\mu'} \psi_{\mu'} \cdot (\underline{\underline{S}}_K)_{\mu',\mu} \tag{320}$$

wherein however utmost two of the matrix-elements $(\underline{\underline{S}}_K)_{\mu\mu'}$ are different from zero. For eg

$$\underline{\underline{S}}_1\,\psi_\mu = \tfrac{1}{2}(\underline{\underline{S}}_1 + i\,\underline{\underline{S}}_2)\,\psi_\mu + \tfrac{1}{2}(\underline{\underline{S}}_1 - i\,\underline{\underline{S}}_2)\,\psi_\mu$$

$$= \tfrac{1}{2}\psi_{\mu-1}\sqrt{(S-\mu+1)(S+\mu)} + \tfrac{1}{2}\psi_{\mu+1}\sqrt{(S-\mu)(S+\mu+1)}$$

where on the right-hande the first is to be accented for $\mu = S$, and the second for $\mu = -S$. on the other hand we have easily

$$\underline{\underline{S}}_3\,\psi_\mu = \psi_\mu \cdot \mu .$$

The Hamilton function will in gensal contain also the S_x besides the x. for eg it might contain an additional term $K(\underline{\underline{S}}_1 H_1 + \underline{\underline{S}}_2 H_2 + \underline{\underline{S}}_3 H_3)$ in an external magnetic field with components H_1, H_2, H_3 and where k denotes the ratio of the magnetic moment and angular momentum of the particle. In general the form of the Hamiltonian must be determined in analogy with the classical theory.

For space relations C_μ and ψ_μ in (316'), transform like the coefficients c_μ and variables Ξ_μ of the invariant form

$$\sum c_\mu \Xi_\mu$$

where according to (305) with $n = 2S$; $k = S - \mu$

$$\Xi_\mu = \frac{\xi_1^{S+\mu}\,\xi_2^{S-\mu}}{\sqrt{(S+\mu)!\,(S-\mu)!}}$$

and ξ_1, ξ_2 transform like as in (303). The transformation of the ψ_μ is accordingly determined directly through the representation (D_S) of the rotation group which is uni- or bi-valued according as S is half integral or integral. For the reflections (308) about the origin, which in contrast to $\underline{S}_k$ are proper skew symmetric tensors which are invariant for the $\underline{S}_k$, the indices of ψ_μ can be allowed unchanged. In the case $S=1$, the functions $\psi_1, \psi_0, \psi_{-1}$, transform by the rotation D^{-1} just like their arguments $-(x_1 - ix_2)$, x_3, $(x_1 + ix_2)$ by the rotation D, so that chosen linear combinations of the ψ_μ can be taken as vector-components.

Of special interest is however the case $S = \frac{1}{2}$ because, as shown by experiments, this leads to the elementary particles (Electron & proton).

Here we have according to (317) (319?)

$$\left(\underline{S}_1 + i\,\underline{S}_2\right)_{+\frac{1}{2},-\frac{1}{2}} = \left(\underline{S}_1 - i\,\underline{S}_2\right)_{-\frac{1}{2},+\frac{1}{2}} = 1$$

and accordingly in matrix notation

$$\underline{S}_1 + i\,\underline{S}_2 = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}; \quad \underline{S}_1 - i\,\underline{S}_2 = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}; \quad \underline{S}_3 = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

accordingly with

$$\underline{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{322}$$

$$\underline{S}_k = \tfrac{1}{2} i\,\underline{\sigma}_k \tag{321}$$

Writing $\psi_\alpha(x,t)$; $\psi_\beta(x,t)$ for $\psi_{+\frac{1}{2}}(x,t)$ & $\psi_{-\frac{1}{2}}(x,t)$ and C_+, C_- for

$C_{+\frac{1}{2}}$ and $C_{-\frac{1}{2}}$, we have

$$\psi(x, \xi_3, t) = C_+ \psi_\alpha(x,t) + C_- \psi_\beta(x,t) \qquad (316'')$$

Further on the basis of (320)

$$\underline{\sigma}_1 \psi_\alpha = \psi_\beta \; ; \; \underline{\sigma}_1 \psi_\beta = \psi_\alpha$$
$$\underline{\sigma}_2 \psi_\alpha = \psi_\beta \cdot i \; ; \; \underline{\sigma}_2 \psi_\beta = \psi_\alpha \cdot (-i)$$
$$\underline{\sigma}_3 \psi_\alpha = \psi_\alpha \; ; \; \underline{\sigma}_3 \psi_\beta = -\psi_\beta$$

and the "density components of the spin moments"

$$\left.\begin{aligned} d_1 &= \psi_\alpha^* \underline{\sigma}_1 \psi_\alpha + \psi_\beta^* \underline{\sigma}_1 \psi_\beta = \psi_\alpha^* \psi_\beta + \psi_\beta^* \psi_\alpha \\ d_2 &= \psi_\alpha^* \underline{\sigma}_2 \psi_\alpha + \psi_\beta^* \underline{\sigma}_2 \psi_\beta = i(\psi_\alpha^* \psi_\beta - \psi_\beta^* \psi_\alpha) \\ d_3 &= \psi_\alpha^* \underline{\sigma}_3 \psi_\alpha + \psi_\beta^* \underline{\sigma}_3 \psi_\beta = \psi_\alpha^* \psi_\alpha - \psi_\beta^* \psi_\beta \end{aligned}\right\} \qquad (323)$$

transform like the components of a vector while

$$\rho = \psi_\alpha^* \psi_\alpha + \psi_\beta^* \psi_\beta \qquad (318')$$

is invariant. The matrices $\underline{\sigma}_k$ satisfy the relations

$$\left.\begin{aligned} \underline{\sigma}_1 \underline{\sigma}_2 &= -\underline{\sigma}_2 \underline{\sigma}_1 = i\sigma_3 \cdots \\ \underline{\sigma}_1^2 &= \underline{\sigma}_2^2 = \underline{\sigma}_3^2 = 1 \end{aligned}\right\} \qquad (324)$$

which are more special than (314) and (315) and signify that they multiply like quaternion units multiplied by i. For space rotations ψ_α, ψ_β transform like the ξ_1, ξ_2 in (303), accordingly ~~after~~ by the matrix

$$\begin{pmatrix} \alpha & -\beta^* \\ \beta & \alpha^* \end{pmatrix}$$

which arises from (307). As already mentioned,

determines the transformation of $(\psi_\alpha, \psi_\beta)$ by infinitesimal rotations.

The case of many particles with spin, which interact, and numbering N, can now be treated without much difficulty. We have to introduce eigen-functions

$$\psi(x_{r1}, x_{r2}, x_{r3}, S_{r3}) \qquad (325)$$

where r the particle index runs from 1 to N. S_{r3} varies from $-S_r$ to $+S_r$. In index notation we have the eigen-functions

$$\psi(x_{rk}, S_{r3}, t) = \sum_{\mu_1 \cdots \mu_N} C_{\mu_1}(S_{13}) \cdots C_{\mu_N}(S_{N3})\, \psi_{\mu_1 \cdots \mu_N}(x_{11} \cdots x_{N3}) \qquad (325')$$

where μ_r runs from $-S_r$ to $+S_r$. In case of only electrons each μ can assume only $+\frac{1}{2}$ & $-\frac{1}{2}$ and (326) defines 2^N functions. An operator $\underline{\underline{S}}_{rk}$ now acts only on one with index μ_r with the same number r and just as in the same way as before.

An essential difference between combined and elementary particles, as also a basis for the value $\frac{1}{2}$ of the spin of the electron result from the relativistic theory.

§ 14. Behaviour of eigenfunctions of many particles for permutations.

Exclusion principle: When we are considered with many particles there are particular relations which depend on the Hamiltonian being invariant for certain exchanges of the particles. When the particles have a spin, the spin coordinates S_{r3} must be exchanged

simultaneously with the position coordinates x_{rK} $(K = 1, 2, 3)$. When the Hamilton operator contains only the space coordinates there arises invariance only in regard to exchanges of these coordinates, and when the spin dependent part of the Hamiltonian is relatively small, the above invariance arises only as an approximation. We shall come back to this situation later; we shall first consider the simultaneous exchange of spin or position variables which gives rise to exact invariance. Let accordingly P be a permutation of N figures 1, 2, ... r, ... N numbering the N equal particles, we obtain from each eigen function $\psi(x_1 \cdots x_{N3}, S_{13} \cdots S_{N3}; t)$, by the application of the permutation P, a new eigen-function belonging to the same observable state of the system given by

$$\psi'(x_{11}, \cdots S_{N3}; t) = P\psi(x_{11} \cdots S_{N3}; t)$$

If any operator, in particular the energy-operator, be symmetrical in the variables, we obtain the same expectation value for it when we calculate this value either with ψ or with ψ'. Only such symmetric operators correspond to observable magnitudes relating to equal particles. On account of the indistinguishability of the particles from each other, there is only one sense in which we can talk of the probability of one of the particles being in the position x_{1K} with spin S_{13}, an other in the position x_{2K} with spin S_{23}, and not however by saying that the first particle is specified by (x_{1K}, S_{13}) the second by (x_{2K}, S_{23}) and so on. The first way is the correct way

$$\sum_P P\,|\psi(x_{11}\cdots s_{N3})|^2\,dx_{11}\cdots ds_{N3} \qquad (326)$$

where the x_{rk} vary in the range dx_{rk} and the spin coordinate s_{r3} varies from $-S$ to $+S$ (for electrons only the numbers $+\frac{1}{2}$ and $-\frac{1}{2}$).

From the general theorems of the previous article it follows that the stationary states of a total system must split up into different systems corresponding to the irreducible representations of the permutation group. Besides, for a symmetric magnitude only those matrix elements for which the initial and end-states have the same term system are different from zero. If the representation be order 1, the term is not degenerate (accidental degeneracy which might arise on account of the invariance of the Hamiltonian under groups other than the permutation one will be left out of account here), and the eigenfunction is multiplied by a numerical factor by the application of the permutation. In general if the representation be of order h, the corresponding energy value is h-fold degenerate. In the corresponding h-dimensional linear vector-space the eigen-functions we can find a basis of orthogonal and normalised eigen-functions $u_1, u_2 \cdots u_h$ such that by a permutation P, the linear manifold $\underline{c}\,(P)$ corresponds to the new eigen functions

$$\underline{\underline{P}}\,u_s = \sum_{r=1}^{h} u_r\, c_{rs}\,(\underline{\underline{P}}) \qquad (327)$$

Since

$$\sum_{sr} \int u_r^* u_s\,dx = \sum_{sr} \int (Pu_r)^*\,(Pu_s)\,dx$$

(s_{r3} appearing in this takes on values from $-S$ to $+S$), the $\underline{\underline{P}}\,u_s$ are also

orthonormal when the u_i's are so, and the representation is unitary. From an arbitrary function $f(q_1 \cdots q_N)$ (where q_r denotes $x_{1r}, x_{2r}, x_{3r}, s_{3r}$ together) one obtains a special function $v(q_1 \cdots q_N)$ transforming itself according to (327), by formation of

$$v(q_1 \cdots q_N) = \sum_P A_{\underline{P}} \cdot \underline{P} f(q_1 \cdots q_N) \tag{328}$$

by properly choosing the numerical coefficients A_P.

Special representations of order 1 are those which belong to symmetric and antisymmetric functions. In the first case

$$\underline{P}\, u(q_1 \cdots q_N) = u(q_1 \cdots q_N); \tag{329}$$

the representation is the identical one ie each group element corresponds to the identity. For the antisymmetric representation we have to distinguish between even and odd permutations. Let $\delta_{\underline{P}} = 1$ for even, and $\delta_{\underline{P}} = -1$ for odd functions, then we have for an antisymmetric function

$$\underline{P}\, u(q_1 \cdots q_N) = \delta_{\underline{P}} \cdot u(q_1 \cdots q_N) \tag{330}$$

Since $\delta_{\underline{P}\cdot\underline{Q}} = \delta_{\underline{P}} \cdot \delta_{\underline{Q}}$; $\delta_{\underline{P}^{-1}} = \delta_{\underline{P}}$; $\delta_{\underline{1}} = 1$,

we have in fact a representation, and for the validity of (330) it is sufficient that u should change sign for the exchange of any two variables. According to (328) we obtain for any arbitrary function f, a symmetric function when all A_P's are put equal to 1

$$v_{\text{symm}}(q_1 \cdots q_N) = \sum \underline{P} f(q_1 \cdots q_N) \tag{328'}$$

and an antisymmetric function when we put $A_{\underline{P}} = \delta_{\underline{P}}$ (= equal to ± 1):

$$v_{antis}(q_1 \cdots q_N) = \sum_{\underline{P}} \delta_{\underline{P}} \underline{P} f(q_1 \cdots q_N) \qquad (328'')$$

when only two particles are present, the symmetric and antisymmetric are the only two unique representations, and the energy value splits up swiftly into these of ~~both~~ the two systems. [The representation can only be of the first order]

If the system contains N-particles with a determinate term-system at one time (corresponding to a certain irreducible representation $\subseteq (\underline{P})$ of the permutation group) it can never be brought to another term-system by external action (force-field, radiation) because the perturbation energy is symmetrical in the ~~energy~~ particles, and its matrix elements with initial states of the considered system, and end states of another system vanish. It also follows as a consequence that the symmetry character of the eigenfunctions of the time-dependent wave equation which are present at the time $t = 0$ remain invariant for all time. One therefore also speaks of non-combining term systems. ~~This however necessitates that the number N of the particles of the sort considered~~ It is however necessary to consider the case where the number N of the particles of the sort considered do not remain constant eg the system might collide with a further particle of the same sort and this requires a special consideration.

Let an atomic system of N electrons be given and let it be assumed

to be in a state with the eigenfunctions $u_\rho(q_1 \cdots q_N)$ belonging to a determined irreducible representation $(D_{(N)})$ of the group Σ_N of permutations of N elements. An $(N+1)^{\text{th}}$ electron might collide with the system; and let the eigenfunctions $U_\rho(q_1 \cdots q_N, q_{N+1})$ of the total system be so chosen before the collision so as to belong to a determinate irreducible representation $D_{(N+1)}$ of the group of permutations of $(N+1)$ elements. Then U_ρ has the form

$$U_\rho = \sum_{\underline{P}} A_{\underline{P}\rho} \, \underline{P} \, u_1(q_1 \cdots q_N) \, v(q_{N+1})$$

where $v(q_{N+1})$ is the eigen-function of the colliding electron and the $A_{\underline{P}\rho}$ are chosen numerical coefficients. The representation $D_{(N)}$ of u must be contained in the $D_{(N+1)}$ of U ~~by the~~ by the reduction with respect to the sub-group Σ_N of Σ_{N+1}. Since further u vanishes rapidly at a great distance R from one of the electrons $q_1 \cdots q_N$, we have very nearly

$$U_\rho(q_1 \cdots q_N, R) = A_{1\rho} \, u_1(q_1 \cdots q_N) \, v(R).$$

After the collision we obtain a new function

$$U'_\rho(q_1 \cdots q_{N+1}) = \sum_{\underline{P}} A'_{\underline{P},\rho} \, \underline{P} \, u'_1(q_1 \cdots q_N) \, v'(q_{N+1})$$

with analogous conditions. Then U_ρ' necessarily belongs to the same representation $D_{(N+1)}$ of Σ_{N+1} as does U_ρ. On the contrary u' can transform itself by application of the permutations $\underline{P}$ of Σ_N

to another representation which might be ~~some~~ other contain any of the irreducible $D_{(N)}$ arising from the reduction of D_{N+1} with respect to the sub-group Σ_N of Σ_{N+1}. These representations are many in general and on account of the collision, the atom might go from one state into another. Only in the two special cases mentioned above does there not appear an ambiguity of the $D^{(R)}_{(N)}$. Accordingly when we are dealing with a symmetric or antisymmetric function $U(q_1 \cdots q_{N+1})$ of the $(N+1)$ particles can we deduce by factorisation

$$\bar{U}_S(q_1 \cdots q_{N+1}) = \sum_P Pu(q_1 \cdots q_N) v(q_{N+1}) = \sum_{k=1}^{N+1} T_{N+1,k}\, \bar{u}_S(q_1 \cdots q_N) v(q_{N+1})$$

$$\bar{U}_a(q_1 \cdots q_{N+1}) = \sum_P \delta_P Pu(q_1 \cdots q_N) v(q_{N+1}) = \sum_{k=1}^{N+1} \delta_k T_{N+1,k}\, \bar{u}_a(q_1 \cdots q_N) v(q_{N+1})$$

where $\bar{u}_s$ and $\bar{u}_a$ are necessarily symmetric and antisymmetric in the N-variables $q_1 \cdots q_N$. Here $T_{N+1,K}$ denotes the exchange (transposition) of two indices $N+1$ and k, $T_{N+1,N+1}$ is accordingly the identity; and $\delta_K = +1$ for $K = N+1$; $\delta_K = -1$ for $1 \leqq K \leqq N$.

Experiments have shown that — so long as we exchange space and spin coordinates simultaneously — for every sort of particles only one class of states appear. This class can be only

the symmetric or the antisymmetric. Experiments further indicate that for the elementary particles (electrons & protons) it is only the antisymmetric class which appears in nature. For other particles for eg. He-nuclei (α-particles) there appears the symmetry class. That wave mechanics allows more, and equally possible correct possibilities than appear in nature is rather curious, and it is to be hoped that a deeper understanding of the elementary particles may bring out a closer knowledge of this narrower choice by nature.

The properties of the symmetry classes follow more clearly when we consider particles which, in the first approximation, are uncoupled ie free from interaction forces. They can however also be found in an external force field. Let in this case, $u_1(q), \ldots u_N(q)$ be the eigen-functions of states in which the N electrons are found, equal states also being permissible. The symmetric eigen-function is the sum of the products

$$U_S(q_1 \ldots q_N) = \sum_P P u_1(q_1) \ldots u_N(q_N) \qquad (331)$$

where the indices of the particle coordinates are permuted for while the indices $1, \ldots N$ of the states are fixed. (For normalization of the

U_S suitable numerical factors are to be chosen). Similarly we find for the antisymmetric function the determinant form

$$U_a(q_1 \cdots q_N) = \sum_P \delta_P P u_1(q_1) \cdots u_N(q_N) = \begin{vmatrix} u_1(q_1) & \cdots & u_N(q_1) \\ u_1(q_2) & \cdots & u_N(q_2) \\ \cdots & \cdots & \cdots \\ u_1(q_N) & \cdots & u_N(q_N) \end{vmatrix} \qquad (332)$$

The antisymmetric eigenfunction vanishes identically when two of the states coincide. ($u_l(q) \equiv u_k(q)$ for $k \neq l$). For antisymmetric states in which particles exist, it cannot therefore happen that two particles find themselves in the same state. This is the content of the Exclusion Principle which was originally formulated ~~by~~ before the setting up of the wave mechanics for electrons; that it is also valid for protons is a result known later on. From the validity of the exclusion-principle for a known species of particles it follows conversely that the particles have antisymmetric states. Because therefore only the antisymmetric eigenfunctions have the property of vanishing when less of the particles are in the same state.

For the possibility without contradiction of excluding all symmetry classes except one it is essential that this kind of symmetry-class should not be noticeable in the region of validity of classical mechanics (geometrical Optics). Let us consider for simplicity

them
only two particles, we can distinguish in principle, by employing the continuity of the variation of their position, when their wave functions $\psi_1(q,t)$ and $\psi_2(q,t)$ nowhere overlap each other ie are different from zero in completely separated regions of space (Strictly speaking separated regions in position-spin-space; we write further for the moment $\int dq$ instead of $\sum_{s_3} \int dx_1 dx_2 dx_3$). In this case

$$\psi_1^*(q_r,t)\,\psi_2(q_r,t) = 0 \qquad r=1,2$$

in the whole of q-space, and over all times under consideration, and hence the expectation value of an arbitrary operator symmetrical in both the particles $\underline{\underline{F}}(\underline{p}_1, \underline{p}_2, \underline{q}_1, \underline{q}_2)$ is given in the symmetric and antisymmetric cases with the eigen-functions (normalised)

$$\left.\begin{aligned} \Psi_s(q_1,q_2,t) &= \frac{1}{\sqrt{2}}\left[\psi_1(q_1,t)\,\psi_2(q_2,t) + \psi_1(q_2,t)\,\psi_2(q_1,t)\right] \\ \Psi_a(q_1,q_2,t) &= \frac{1}{\sqrt{2}}\left[\psi_1(q_1,t)\,\psi_2(q_2,t) - \psi_1(q_2,t)\,\psi_2(q_1,t)\right] \end{aligned}\right\} \qquad (331')$$

by

$$\bar{F}(t) = \int \Psi_s^*\, \underline{\underline{F}}\, \Psi_s\, dq_1 dq_2 = \int \Psi_a^*\, \underline{\underline{F}}\, \Psi_a\, dq_1 dq_2$$

$$= \int \psi_1^*(q_1,t)\,\psi_2^*(q_2,t)\left[\underline{\underline{F}}\,\psi_1(q_1,t)\,\psi_2(q_2,t)\right] dq_1 dq_2$$

$$= \int \psi_1^*(q_2,t)\,\psi_2^*(q_2,t)\left[\underline{\underline{F}}\,\psi_1(q_2,t)\,\psi_2(q_1,t)\right] dq_1 dq_2$$

since, in this case, (at least when $\underline{\underline{F}}$ is rational integral in $\underline{p}$)

$$\psi^*(q,t)\,\psi^*(q,t)\left[\underline{\underline{F}}\,\psi(q_1,t)\,\psi(q,t)\right] = 0$$

It is sometimes usual to express the fact that the electrons satisfy the exclusion principle ie have antisymmetric states by saying that all electrons "have (concluded) a treaty with each other" or "know of each other" We see however that this "treaty", if we might say so, enters automatically into action when the wave packets of the electrons overlap each other ie when the possibility that both can be found at the same point in position-spin space is not excluded from consideration (however without regard to symmetry classes).

We shall now consider the behaviour of many electrons a little more ~~exactly~~ in detail by separating out the space and spin coordinates. In many cases it is allowed to consider the interaction between spin or orbit ie between certain parts of the Hamiltonian containing the spin operators as small when compared with the interaction of the electrons. In the zeroth approximation (each electron moving in identical external fields) the Hamiltonian has the form

$$\underline{\underline{H}}^{(0)} = \sum_{r=1}^{N} \underline{\underline{H}}_r^{(0)}$$

where each $\underline{\underline{H}}_r^{(0)}$ acts only on the space-coordinates of the rth electron. In the first approximation there appears a perturbation

$$\underline{\underline{H}}^{(1)} = \sum_{r,s}{}' \frac{e^2}{r_{rs}}$$

Coulomb interaction energy of the particles already introduced in (98), (99). In the second approximation enters the interaction energy between spin and orbit given by

$$\underline{\underline{H}}^{(2)} = V(x_{rk}, s_{r3}).$$

When $\underline{\underline{H}}^{(2)}$ can be supposed considered as small, not only when compared with $\underline{\underline{H}}^{(0)}$ but also relative to $\underline{\underline{H}}^{(1)}$, one speaks of the Russell-Saunders coupling.

The behaviour of eigenfunctions corresponding to these assumptions can be discussed more closely in the simplest case of two particles. The antisymmetric solutions for the total ie in the spin- and space coordinates together are given ~~by~~ in the zero and first approximation (omitting the index $k = 1, 2, 3$ for the three space coordinates of each particle) according to (31b") by

$$\left.\begin{aligned} u(x_1, s_{13}) &= u(x)\left[a_\alpha C_+(s_3) + a_\beta C_-(s_3)\right] \\ v(x_2, s_{23}) &= v(x)\left[b_\alpha C_+(s_3) + b_\beta C_-(s_3)\right] \end{aligned}\right\} \qquad (333)$$

with

$$U(x_1, x_2, s_{13}, s_{23}) = u(x_1, s_{13})\, w(x_2, s_{23}) - u(x_2, s_{23})\, v(x_1, s_{13})$$

Here is expressed the fact that in the zero and first approximation the spin and space variables are separable; $u(x)$ and $v(x)$ are the

states considered. If both are in the same state relative to the space coordinates one has to put $u(x) = v(x)$. If originally no external field is present, the Hamilton-operator is rotation-invariant as we shall assume and we obtain allowed eigen-functions for an arbitrary choice of $a_\alpha, a_\beta, b_\alpha, b_\beta$. Then $U(x_1, x_2, s_{13}, s_{23})$ is a linear combination of the following four (mutually orthogonal and normalised) eigen-functions

$$U^I(x_1, x_2, s_{13}, s_{23}) = \frac{1}{\sqrt{2}}\left[u(x_1)\,v(x_2) - u(x_2)\,v(x_1)\right] A_{m_s}(s_{31}, s_{32})$$

with $m_s = -1, 0, +1$ and

$$A_{-1}(s_{13}, s_{23}) = C_-(s_{13})\,C_-(s_{23})$$

$$A_0 = \frac{1}{\sqrt{2}}\left[C_+(s_{13})\,C_-(s_{23}) + C_-(s_{13})\,C_+(s_{23})\right]$$

$$A_{+1} = C_+(s_{13})\,C_+(s_{23})$$

and also

$$U^{II}(x_1, x_2, s_{13}, s_{23}) = \frac{1}{\sqrt{2}}\left[u(x_1)\,v(x_2) + v(x_1)\,u(x_2)\right] \times$$
$$\times \frac{1}{\sqrt{2}}\left[C_+(s_{13})\,C_-(s_{23}) - C_-(s_{13})\,C_+(s_{23})\right].$$

We see that the spin eigenfunctions which appear here as factors are symmetric in the first case, and antisymmetric in the second. In the second case the application of the operator $\underline{\underline{S}}_k = \underline{\underline{S}}_{1k} + \underline{\underline{S}}_{2k}$ to the spin eigenfunction gives the value zero. [use $(\underline{\underline{S}}_{1k})\,C_\mu = \sum_{\mu'} C_{\mu'}\,(\underline{\underline{S}}_k)_{\mu'\mu}$] It therefore follows readily that there are 4

transformations which act likewise on $C_+(S_{13})\,C_-(S_{23})$ and $C_+(S_{23})\,C_-(S_{13})$, the spin eigen-function in the second case is multiplied by the determinant of the transformation. This determinant has, as we have seen before, the value 1 for transformations of $C_+\,C_-$ corresponding to rotations. To $\overline{U}^{II}$ therefore corresponds one term with $S = 0$ (eigen-value of spin operator or eigen-value of the corresp. to the spin eigenfunction $= 0$) Even when many u and v correspond to the same eigen-value (non-vanishing resultant angular momentum L of orbital motion) it follows from the invariance of the Hamiltonian for rotations that the insertion of a perturbation energy $\underline{\underline{H}}^{(2)}$ does not bring out about any separation of the term. In the case $u(x) = v(x)$ the first normalisation factor of $\overline{U}^{II}$ is to be replaced by $\frac{1}{2}$ and the factor is simply written as $u(x)\cdot v(x)$. In the first approximation ie by neglection of $\underline{\underline{H}}^{(2)}$, the term perturbation corresponding to $\overline{U}^{II}$ is

$$\Delta E_{II} = J_0 + J_1 \qquad (334\,a)$$

where
$$\left.\begin{aligned} J_0 &= \int |u(x_1)|^2\,|v(x_2)|^2\,V(x_1 x_2)\,dx_1\,dx_2 \\ J_1 &= \int u^*(x_1)\,u(x_2)\,v^*(x_1)\,v(x_2)\,V(x_1 x_2)\,dx_1 dx_2 \end{aligned}\right\} \qquad (335)$$

J_1 is the socalled exchange integral.

[The perturbation gives $\Delta E = -\Omega_{KK}$ and in the first approximation Ω is to be taken $V(x_1, x_2)$ and the expectation value is derived from the space part only of $\overline{U}_{II}$. This gives J_0 and J_1 by observing that the term in the integrand of each

$$\underline{\underline{S}}_K = \underline{\underline{S}}_{1K} + \underline{\underline{S}}_{2K} = \frac{1}{2}\left(\underline{\underline{\sigma}}_{1K} + \underline{\underline{\sigma}}_{2K}\right) = \frac{1}{2}\underline{\underline{\sigma}}_K$$

operating by $\underline{\underline{S}}_K$ on the spin eigen-function of U^{II}, say $K = 1$, we have

$$\underline{\underline{S}}_1 \cdot \frac{1}{\sqrt{2}}\left[C_+(S_{13})\,C_-(S_{23}) - C_-(S_{13})\,C_+(S_{23})\right]$$

$$= \frac{1}{2}\left(\underline{\underline{\sigma}}_{11} + \underline{\underline{\sigma}}_{21}\right)\left[\psi_\alpha^{(1)}\psi_\beta^{(2)} - \psi_\beta^{(1)}\psi_\alpha^{(2)}\right]$$

$$= \psi_\beta^{(1)}\psi_\beta^{(2)} + \psi_\alpha^{(1)}\psi_\alpha^{(2)} - \psi_\alpha^{(1)}\psi_\alpha^{(2)} - \psi_\beta^{(1)}\psi_\beta^{(2)} = 0$$

Similarly for $\underline{\underline{S}}_2$ and $\underline{\underline{S}}_3$.

In the case of A_-, A_0, A_+ of the eigenfunction U^I

$$\underline{\underline{S}}_3(A_-) = \frac{1}{2}\underline{\underline{\sigma}}_3(A_-) = \frac{1}{2}\underline{\underline{\sigma}}_3\left(\psi_\beta^{(1)}\psi_\beta^{(2)}\right) = \frac{1}{2}\left(-\psi_\beta^{(1)}\psi_\beta^{(2)} - \psi_\beta^{(1)}\psi_\beta^{(2)}\right) = -1$$

Similarly $\underline{\underline{S}}_3(A_+) = +1\,(A_+)$; and $\underline{\underline{S}}_3(A_0) = 0$.

Since m_s takes values $-1, 0, +1$, the corresponding value for $j = 1$ (ie total

Thus each non-relativistic level of the orthohelium corresponding to azimuthal quantum number L can be split up, taking spin-orbit coupling into consideration, into a triplet with the inner quantum numbers $J = L+1, L, L-$

This corresponds to splitting the reducible representation $D_1 \times D_2$ into the irreducible parts D_J with $J =$ the above three values. (for $L =$ there is no splitting up)

is the sum of two terms each of one of which is obtained from the other by interchanging x_1 and x_2 ·].

In the first case, corresponding to the eigenfunctions U^I the spin eigen-functions are symmetric · The A_{-1} , A_0 , A_{+1} transform into each other for rotations · This depends in the last analysis on the fact that rotations and permutations are commutative, and the symmetry character is not altered by rotations · The eigen-functions A_{-1} , A_0, A_{+1} of the spin alone correspond to the values $-1, 0, +1$ of the quantum number m_s of the three components $S_3 = S_{13} + S_{23}$ of the resulting spin moments, and the value $S = 1$ of the quantum number of the magnitude of the resulting spin moment · The corresponding eigenvalue perturbation is in the first approximation

$$\Delta E_I = J_0 - J_1 \qquad (346)$$

where J_0 and J_1 are the integrals in (335). If L be the orbital angular momentum there appears in general, as a consequence of the perturbation energy $\underline{\underline{H}}^{(2)}$ a further splitting up of the terms because the reducible representation

$$D_1 \times D_2$$

of the rotation group splits up into its irreducible parts

$$D_J$$

with $J = L+1, L, L-1$ · for $L = 0$ (S-term) obviously no splitting up enters. We have accordingly to do here with a triplet system. It is to be noticed

that for $u(x) = v(x)$ the eigen-function identically vanishes.

The essential result is the following: The exclusion-principle so acts that for two electrons whose symmetrical states in only the space coordinates belong correspond to the singulet-terms, while antisymmetric states in the same coordinates correspond to the triplet terms. By neglecting the interaction energy between spin and space coordinates these terms are distinguished energetically by means of the exchange integral.

[The term system of Helium and of ions with two electrons arises from two term systems one system of triplet terms (Orthohelium) and another system of singulet terms (Parhelium) which do not optically combine with each other]

This is the essential content of Heisenberg's theory of the Helium spectrum. On account of the indistinguishability of the electrons the mutual place of two electrons is never distinguishable from each other in principle. By "exchange" of electrons in the He-atom the most that is observable in principle is that the spins of the outer and inner electrons which are directed oppositely in one case might experience interchange in course of time.

The theory can be generalized from two to an arbitrary number N of electrons. We shall here merely sketch the results without trying to prove them. without going to into the general theory of representations of the permutation

group, it can be seen that, as a consequence of the exclusion principle, although the symmetry of eigenfunctions in the space coordinates alone is only a smaller part of all the possible representations which might occur. It is only necessary to substitute for the $u_n(q)$ in the determinant (332) expressions of the form (333) and then resulting to order the resulting expression. It is thereby shown that the result of applying the operators $\underline{\underline{S}}^2 = \sum_{k=1}^{3} \sum_{r=1}^{N} \underline{\underline{S}}_{rk}^2$ to the spin eigen-functions, which always multiplies them by a number of the form $S(S+1)$, determines uniquely the symmetry character of the spin, and on account of the exclusion principle also that of the space eigen-functions. Hence it follows that for the Russell-Saunders coupling (smallness of $\underline{\underline{H}}^{(2)}$ relative to $\underline{\underline{H}}^{(1)}$) in case of N-particles also, the terms in different multiplets which are distinguished transform into each other as is distinguished by linear combinations of exchange integrals.

It is to be noticed further that the application of the earlier Considerations on collisions to the symmetry of eigen functions for exchange of space coordinates alone, shows that, by the neglection of the spin forces for the collision of an electron with an atom, the atom can be transformed so as to have a term with a different multiplicity from its original term. Because in this case we can have other classes of symmetry, other than the symmetric and antisymmetric, also appearing.

It remains further to speak of statistical applications characteristic

for systems of many similar particles ~~is~~ a definite symmetry class (symmetric or antisymmetric). Let us consider a large number of force free particles in a closed volume V so that the eigen-functions are stationary plane waves. The number of stationary states of a particle which lies in the volume element $p_K, p_K + dp_K$ $(K = 1, 2, 3)$ of momentum space is then

$$Z = V \cdot \frac{1}{h^3} dp_1 dp_2 dp_3$$

For particles with spin there appears further the weight factor $g = 2s+1$ ($g = 2$ for electrons and protons) which for the sake of simplicity we shall here not consider in the first instance. It is then useful not to consider a single state but a group of Z states of the concerned kind with Z a very large number. On the other hand the energy of the particles inside the group shall be so slightly varied that the Boltzmann factor $e^{-E/KT}$ shall be sensibly constant for the group of states. The question then is about the a priori probability W that N particles lie in this group of states. According to general principles this is the number of stationary states of the total system of N-particles in which any one particle has a momentum between p_K & $p_K + dp_K$. This number depends upon the symmetry class and is different from its value in the case of independent particles for which, simply,

$$W = Z^N \qquad (336)$$

For particles with symmetric states the situation is quite different. The case that the particle is in state 1, the second particle in state 2,

state 2 correspond to only <u>one</u> state of the system of two particles, and accordingly it is ~~a priori~~ apriori equally probable that of two particles <u>one</u> is in state 1 and the other in state 2, as that both are in the same state 1 or 2. For independent particles however the probability for the second possibility is only half as great as that of the first possibility. In general, the symmetric eigen-function for N-particles is characterised by specifying <u>how many</u> of the N molecules are found in each of the Z-states of the group. We will call such a result a "factorisation form". We find the number of the factorisation form as

$$W = \frac{(N+Z-1)!}{N!\,(Z-1)!} \qquad \text{(Symmetric states)} \qquad (336a)$$

[This is the number of combinations of Z things taken N at a time repetitions being allowed]

In the case of antisymmetric eigenfunctions (exclusion principle) we have to strike out from the above number all those in which there are particles more than one in each state. We then find

$$W = \frac{Z!}{N!\,(Z-N)!} \qquad \text{(antisymmetric states)} \qquad (336b)$$

[Number of combinations of Z things taken N at a time repetitions not being allowed]

where necessarily $N \leq Z$. If we have many groups of states for each

to the product of the numbers W for the individual groups. (For independent particles there comes in further the factor $N!/N_1!\,N_2!\ldots$, where N_n is the number of particles in individual groups, while $N = \sum_n N_n$ is the total number of particles. For particles with spin these W are simply to be raised to the power g, if N denotes the number of particles with determined spin states).

Before the knowledge of the symmetry properties of the eigenfunctions of N particles, the numbering of symmetry states appeared to have been chosen on the basis of a special assumption. It was shown by Bose that by considering radiation as a gas consisting of corpuscular light quanta correct results could be obtained. This was applied by Einstein to the case of material gases. One therefore often speaks of Einstein-Bose statistics. It does not however deal with any new kind of statistics since, as we now know, the apriori probability is always proportional to the number of concerned states of the total system. We can therefore simply speak of the statistics of ~~stationary~~ symmetric states. It is to be applied to such material particles, like α-particles for eg, which possess symmetric states. For particles following the exclusion principle, the statistical consequences have been worked out by Fermi, and independently by Dirac who has based his considerations on properties of antisymmetric eigen-functions. When one speaks often of Fermi-Dirac statistics, we mean

the statistics of antisymmetric states.

We shall now speak of an application of both these ~~exact~~ kinds of statistics since it can be formulated without going into questions of thermal equilibrium. It is concerned with ~~with~~ the totality of N force free particles of a determinate velocity interval and the fluctuations of the number of particles and their energy in a part of the volume. The relations for the number of particles is ~~simply~~ simpler, and we shall deal with it first. If x_ν be an abbreviation for the space coordinates of the νth particle, then

$$n(x_1, \cdots x_N) = \sum_{\nu=1}^{N} \int_v dx\, \delta(x - x_\nu)$$

is equal to the number of those x_ν in the considered part volume v, over which the integral is taken. Then we have

$$\bar{n} = \int n(x_1 \cdots x_N) \left| U(x_1 \cdots x_N) \right|^2 dx_1 \cdots dx_N$$

$$\overline{n^2} = \int n^2(x_1 \cdots x_N) \left| U(x_1 \cdots x_N) \right|^2 dx_1 \cdots dx_N$$

where $U(x_1 \cdots x_N)$ denotes the eigen-function. The integral can be worked out. If we have to do with the considered group of Z states where Z is a large number, and every state of the total system is considered equally probable in the group, and if further we restrict ourselves to the case where the volume v is small compared with the total volume, we can deduce the well known result (with $z = Zv/V$)

$$\overline{(\Delta n)^2} = \overline{n^2} - (\bar{n})^2 = \bar{n} + \frac{\bar{n}^2}{z} \quad \text{for sym. states} \qquad (338a)$$

$$\overline{(\Delta n)^2} = \overline{n^2} - (\bar{n})^2 = \bar{n} - \frac{\bar{n}^2}{z} \quad \text{for antisymm. states} \qquad (338b)$$

[This calculation is due to R. Peierls. Appears difficult].

For independent particles, on the other hand it is well known that $\overline{(\Delta n)^2} = \overline{n}$. It is important to remark that here terms quantities of order $1/z$ relative to the terms written here have been omitted.

For the corresponding question of energy in a partial volume some caution is enjoined since the knowledge of the momentum of a particle means that the position is known only with a certain uncertainty. In contrast to the measurement of number of particles in a partial volume, the energy can only be determined by inserting walls (potential barriers) or other analogous external influence which is conditioned by the limiting off of the partial volume. According to this connection with potential barriers the energy in the part volume essentially corresponds to the energy which was, before the connection, in a volume whose boundaries were undetermined with respect to the order of magnitude of the wave length of material waves. only when the part volume is large when compared with the mean wave length has the question about the energy in the part any determinate meaning. According to Heisenberg this method must be observed when one has to eliminate certain singularities which first of all appear, if the energy in a part volume can be written as

$$\underline{\underline{E}} = \frac{1}{2m} \sum_r \underline{\underline{p}}_r D(\underline{\underline{x}}_r) \underline{\underline{p}}_r \quad ; \quad D(x) = \int_v \delta(x - x'_\rho)\, dx'$$

The singularities however vanish when one substitutes for $D(x)$ a continuous

function. ie introduces a weight function which is steep but vanishes continuously outside the considered region v, and thus forms

$$\int_v G(x')\,\delta(x-x')\,dx' = G(x)$$

and $$E = \frac{1}{2m}\sum_r \underline{\underline{p}}_r\, G(\underline{\underline{x}}_r)\,\underline{\underline{p}}_r$$

Then analogous to (338) we get

$$\overline{(\Delta E)^2} = \overline{E^2} - \overline{E}^2 = \frac{1}{2m}\,p^2.\,\overline{E} + \frac{\overline{E}^2}{2} \quad \text{for sym. states} \qquad (339a)$$

$$\overline{(\Delta E)^2} = \overline{E^2} - \overline{E}^2 = \frac{1}{2m}\,p^2.\,\overline{E} - \frac{\overline{E}^2}{2} \quad \text{for antisym.} \qquad (339b).$$

We must here mention a special mathematical method due to Jordan and Klein (case of sym. states) and Jordan and Wigner and which can be considered as repeated (double) quantisation of waves in ordinary three dimensional space. This method is understood by considering the analogy between material particles in symmetrical states on one side and the light quanta of radiation on the other. It is doubtful whether it really deals with an actually deep physical analogy, and it can also be seen that all results of wave mechanics can be obtained without applying the method. However, at least as a method of calculation it must be dealt with.

In § 9 we have denoted by $C_n^* C_n$ the probability that a particle can be found in the state described by the eigen-function $u_n(x)$. Let us now introduce the time-dependent operators (matrices) α_n^* and α_n which

satisfy the V-R.

$$\underline{\underline{\alpha}}_n \underline{\underline{\alpha}}_m^* - \underline{\underline{\alpha}}_m^* \underline{\underline{\alpha}}_n = \begin{cases} 0 & , \quad n \neq m \\ 1 & \quad n = m \end{cases} \tag{340}$$

while

$$\underline{\underline{\alpha}}_n \underline{\underline{\alpha}}_m - \underline{\underline{\alpha}}_m \underline{\underline{\alpha}}_n = 0 \; ; \; \underline{\underline{\alpha}}_n^* \underline{\underline{\alpha}}_m^* - \underline{\underline{\alpha}}_m^* \underline{\underline{\alpha}}_n^* = 0 \tag{340'}$$

Here $\underline{\underline{\alpha}}^*$ denotes always the operator hermitian-conjugate to $\underline{\underline{\alpha}}$. Then it is easy to see that the eigen-values of

$$\underline{\underline{\alpha}}_m^* \underline{\underline{\alpha}}_n = \underline{\underline{N}}_m \tag{341}$$

are the positive integers $0, 1, 2, \ldots$ Writing $\underline{\underline{N}}_m$ as diagonal matrix the matrices of $\underline{\underline{\alpha}}_m^*$ and $\underline{\underline{\alpha}}_m$ are

$$\left(\underline{\underline{\alpha}}_m^*\right)_{N_m N_m'} = \begin{cases} \sqrt{N_m} & \text{for } N_m' = N_m - 1 \\ 0 & \text{otherwise} \end{cases} \tag{342,a}$$

$$\left(\underline{\underline{\alpha}}_m\right)_{N_m N_m'} = \begin{cases} \sqrt{N_m + 1} & \text{for } N_m' = N_m + 1 \\ 0 & \text{otherwise} \end{cases} \tag{342'a}$$

Accordingly $\underline{\underline{\alpha}}_m^*$ as an operator applied to a function $f(N_m)$ transforms it into $\sqrt{N_m + 1}\, f(N_m + 1)$, and $\underline{\underline{\alpha}}_m f(N_m)$ goes over to $\sqrt{N_m}\, f(N_m - 1)$. Putting

$$\underline{\underline{\alpha}}_m^* = \sqrt{\underline{\underline{N}}_m}\, \underline{\underline{\Delta}}_m^* \; ; \; \underline{\underline{\alpha}}_m = \underline{\underline{\Delta}}_m \sqrt{\underline{\underline{N}}_m} \tag{343}$$

where,

$$\underline{\underline{\Delta}}_m^* \underline{\underline{\Delta}}_m = 1 \tag{344a}$$

[one often writes $\Delta_m = e^{\frac{i}{\hbar}\theta_m}$ so as to satisfy (344a) identically]

we ~~also~~ have,

$$\left.\begin{aligned} \underline{\underline{\Delta}}\, f(N_m) &= f(N_m + 1) \\ \Delta^* f(N_m) &= f(N_m - 1) \end{aligned}\right\} \tag{345a}$$

According to Jordan and Wigner exactly analogous V-R can be set up for particles with antisymmetric states, where the N_n can have only the values 0 and 1. According to these authors we can put

$$\underline{\underline{\alpha}}_n \underline{\underline{\alpha}}_m^* + \underline{\underline{\alpha}}_m^* \underline{\underline{\alpha}}_n = \begin{cases} 0 & \text{for } n \neq m \\ 1 & \text{for } n = m \end{cases} \tag{340b}$$

$$\underline{\underline{\alpha}}_n \underline{\underline{\alpha}}_m + \underline{\underline{\alpha}}_m \underline{\underline{\alpha}}_n = 0 \,, \quad \underline{\underline{\alpha}}_n^* \underline{\underline{\alpha}}_m^* + \underline{\underline{\alpha}}_m^* \underline{\underline{\alpha}}_n^* = 0 \,, \text{ for } m \neq n \tag{340'b}$$

where further

$$\underline{\underline{\alpha}}_n^* \underline{\underline{\alpha}}_n = \underline{\underline{N}}_n \tag{341'}$$

The matrices now would be

$$(\alpha_n^*)_{1,0} = \epsilon_n \,, \quad (\alpha_n)_{0,1} = \epsilon_n \,, \quad (\alpha_n^*)_{N_n N_n'} = (\alpha_n)_{N_n' N_n} \tag{342b}$$

where $\epsilon_n = \pm 1$ the sign to be further determined depending on n. To decide about this sign, we shall think of the states n as brought into a determined order. We can thus put

$$\epsilon_n = \prod_{m \leq n} (1 - 2N_m) \tag{346}$$

and take this equal to ± 1 according as the number of any <u>occupied</u> state, which lies before the considered state, is even or odd. We have then to put.

$$\left.\begin{aligned} \underline{\underline{\alpha}}_n^* f(N_1 \cdots 0_n \cdots) &= \epsilon_n (N_1 \cdots 0_n \cdots) f(N_1 \cdots 1_n \cdots) \\ &= -\epsilon_n (N_1 \cdots 1_n \cdots) f(N_1 \cdots 1_n \cdots) \\ \underline{\underline{\alpha}}_n^* f(N_1 \cdots 1_n \cdots) &= 0 \end{aligned}\right\} \tag{345b}$$

$$\left.\begin{aligned} \underline{\underline{\alpha}}_n f(N_1 \cdots 0_n \cdots) &= 0 \\ \underline{\underline{\alpha}}_n f(N_1 \cdots 1_n \cdots) &= \epsilon_n (N_1 \cdots 0_n \cdots) f(N_1 \cdots 0_n \cdots) \\ &= -\epsilon_n (N_1 \cdots 1_n \cdots) f(N_1 \cdots 0_n \cdots) \end{aligned}\right\} \tag{345'b}$$

From the $\underline{\underline{\alpha}}_n$, $\underline{\underline{\alpha}}_n^*$ we can easily go over to the Ψ-functions according to

$$\underline{\underline{\Psi}}(q) = \sum_n \underline{\underline{\alpha}}_n(t)\, u_n(q) \;;\quad \underline{\underline{\Psi}}^*(q) = \sum_n \underline{\underline{\alpha}}_n^*(t)\, u_n^*(q) \tag{346}$$

where q stands for the space and spin coordinates, and the u_n, u_n^* are ordinary numbers and form a normalised orthogonal system. This last fact leads to the V-R analogons to (342, a, b)

$$\underline{\underline{\Psi}}(q)\,\underline{\underline{\Psi}}^*(q') \mp \underline{\underline{\Psi}}^*(q')\,\underline{\underline{\Psi}}(q) = \delta(q-q')\,\underline{\underline{1}} \tag{347}$$

$$\underline{\underline{\Psi}}^*(q)\,\underline{\underline{\Psi}}^*(q') \mp \underline{\underline{\Psi}}^*(q')\,\underline{\underline{\Psi}}^*(q) = 0 \;;\quad \underline{\underline{\Psi}}(q)\,\underline{\underline{\Psi}}(q') \mp \underline{\underline{\Psi}}(q')\,\underline{\underline{\Psi}}(q) = 0 \tag{347'}$$

where the upper and lower signs hold respectively for the symmetric or antis-symmetric states. $\delta(q-q')$ stands for $\delta(x-x')\,\delta_{\mu\mu'}$ where $\delta_{\mu\mu'}$ is the ordinary δ-symbol for discrete spin-coordinates.

As applications of this method we can calculate the energy and density fluctuations, which can be written as

$$n = \sum_{s_3} \int \underline{\underline{\Psi}}\,\underline{\underline{\Psi}}^*\, dx$$

$$E = \sum_{s_3} \int \frac{\hbar}{2m} \frac{\partial \underline{\underline{\Psi}}}{\partial x} \frac{\partial \underline{\underline{\Psi}}^*}{\partial x}$$

and the mean value (expectation value) of n, n^2 or E, E^2 formed over the considered groups of states gives the same result as that calculated in configuration space.

This is a special case of the general equivalence of the method of quantised eigen-frequencies and the method of configuration space which — as many well-known authors have shown — can be extended even to the problem of equivalent particles with interaction forces.

Let

$$\underline{\underline{H}} = \frac{1}{2m} \sum_r \left[-\hbar^2 \frac{\partial^2}{\partial x_r} + \sum_r V_r(q_r) + \sum_{r<s} \Omega(q_r, q_s) \right] \tag{348}$$

be the Hamiltonian operator. The external forces are here represented by $V(q_r)$ and the function Ω depending on a pair of particles describes the interaction. For the Coulomb interaction forces $H_{rs} = e^2/r_{rs}$; in view of further generalisations concerning magnetic interactions of particles we shall allow V and Ω to depend on spin coordinates also. If we think of $\rho(q) = \psi^*(q)\psi(q)$ as the classical Charge-cloud (swarm), we can write the interaction energy of the rth and s^{th} particles classically as

$$\iint dq_r\, dq_s\, \Omega(q_r q_s)\, \rho(q_r)\, \rho(q_s)$$

Analogously the Hamiltonian operator has to be defined by

$$\left.\begin{aligned} \underline{\underline{H}} = \frac{1}{2m} \sum_{s_3 r} \int \left[\hbar^2 \frac{\partial \underline{\underline{\Psi}}^*}{\partial x_r} \frac{\partial \underline{\underline{\Psi}}}{\partial x_r} + V(q_r)\, \underline{\underline{\Psi}}^* \underline{\underline{\Psi}} \right] dx_r \\ + \sum_{s_3 r,\, s_3 s} \iint \underline{\underline{\Psi}}^*(q')\, \underline{\underline{\Psi}}^*(q)\, \Omega(q, q')\, \underline{\underline{\Psi}}(q')\, \underline{\underline{\Psi}}(q)\, dq\, dq' \end{aligned}\right\} \tag{348'}$$

where $\underline{\underline{\Psi}}^* \underline{\underline{\Psi}}$ are the operators which, according to (346), can be expressed in terms of the operators $\underline{\underline{\alpha}}_r^* \underline{\underline{\alpha}}_s^*$ by developing Ψ in a suitable orthogonal system. Let us introduce the number N_n of particles in a defined state n of this system as the variable of a wave function $\Phi(N_1, N_2, \ldots t)$, on which the operator (348') works; we can then set up a wave equation according to

$$-\frac{\hbar}{i} \frac{\partial \Phi}{\partial t} = \underline{\underline{H}}\, \Phi(N_1, N_2, \ldots t) \tag{349}$$

It is seen therefore that the deductions from this wave equation are completely

coincident with the deductions from the wave equation in configuration space to which belongs the Hamilton-operator (348). This is true both for particles with symmetrical as well as antisymmetrical states. For this coincidence the order of factors in (348') is essential.

For the case of particles of many kinds (for eg. electrons & protons) we can introduce special $\underline{\underline{\Psi}}$-operators for each kind such that the $\underline{\underline{\Psi}}$-operators for different kinds commute with each other.

This is, shortly sketched, the method of quantised eigen-vibrations. It is to be emphasised that in spite of the formal mathematical analogy an essential physical distinction exists between the transition from the magn classical magnitudes p, q to the wave-mechanical operators $\underline{\underline{p}}$, $\underline{\underline{q}}$ on the one hand, and the one from the functions ψ^*, ψ in ordinary space to the operators $\underline{\underline{\Psi}}^*$, $\underline{\underline{\Psi}}$ on the other; this is because the functions ψ^*, ψ are symbolic magnitudes not directly observable by themselves, and contain the quantum of action.

§ 15.

Errors in Pauli. (1)

p. 87. Eqn (6) should be $\omega_0 = mc^2/\hbar$ and not $\omega_0 = mc/\hbar$

p. 91. In the first equation (15) replace m_0 by m since m is the notation used for rest mass

p. 93. Eqn (21)$_3$ on the right side have Δp_x in place of $\Delta p_x'$.

p. 95. In eqns (24'*) and (24''*) write $-i$ in place of i

" Eqn (6) ought to be $E_0 = \hbar\omega_0 = mc^2$

96. Throughout this page read eqn (29) for eqn (25)

" In second line, third paragraph read $W(x_i)$ for $W(R_i)$

97. In this page (eqns (25), (25*) should be (29), (29*).

p. 99. In the first ~~equation~~ expression in the line preceding eqn (42) $\frac{\partial}{\partial p}$ should be $\frac{\partial}{\partial p_\ell}$.

" In eqn (47), middle term read $F(x_\ell)$ in place of $F(x)$

" " (47'), " read $\partial/\partial x_\ell$ " $\partial/\partial x_i$

100. Write $p_x' = p_x - mv$ instead of $p_x' = p_x - mv_x$ since here v_x is v itself

" In the eqn below this have φ' in place of φ on the right hand side

" In the differential eqn below eqn (49') on the right hand side write $\left(E_0 - \frac{\hbar^2}{2m}\Delta'\right)\psi'$ instead of $E_0 - \frac{\hbar^2}{2m}\Delta'$

101. In deriving eqn (51), it is assumed that $x_0 = 0$ & this is not stated.

" In the second line above (52') put $\hbar/2\pi i$ for $\hbar/2m$ in the factor for $\vec{i}$ and inside the bracket he write ψ_0^* in the first term.

" In the line above this is $\overline{(x^2)}_0 = \int x^2 \psi_0^* \psi_0 \, dV$ and not $\int x \psi_0^* \psi_0 \, dV$.

2. In the third line ~~from~~ of the expression for D multiply first term by $\psi^*\psi$ + second term by $\frac{1}{2}$

the eqn $\overline{p^2}\,\overline{x^2} = \cdots \geqq \hbar^2/4$ is to be marked as (54)

. The operator $\underline{H}(\psi) = i\psi \frac{\partial \psi^*}{\partial x}$ given is not correct, and has to be replaced by $i\psi p^* \frac{\partial \psi}{\partial x}$.

. About the middle of the page $\sum m \frac{d\bar{x}_k}{dt} = \cdots = \cdots = \left(\frac{\partial H}{\partial p_k}\right)$, the last eqn must be $\left(\frac{\partial H}{\partial p_k}\right)$.

07. In the line below eqn (70) first term should read $\frac{d\bar{x}_k}{dt}$ and third term as $\bar{p}_k/m$

08. In eqn (71) and the one above it, insert the mass m on the left hand side i.e. $\frac{1}{2} m \frac{d^2}{dt^2} \overline{(\Delta x_k)^2}$.

" (74) first line there should be no factor $\frac{1}{c}$ for second term

In the first footnote, last line but one read $\dot{x}_2 H_{12} - \dot{x}_3 H_{31}$ and also $H_{31} = -H_{13}$

9. Eqn (77') first term should have the factor $\frac{\hbar}{2mi}$ instead of $\frac{h}{2m}$.

" (79) first line, second factor in the first term within brackets should read $\frac{\partial \psi}{\partial x_{1k}} - \frac{ie}{\hbar c} \Phi_k \psi$

In the expression for $\int T_{kk} dV$ replace h by $\hbar$

In the equation after (95), (N) is to be replaced by (f).

5th line of 2nd paragraph read $V^{(a)}$ in place of $V^{(a)}$,

In eqn (102') in the left hand side of the first equation replace ψ by φ.

Eqn (104) - right hand side must have the integrand as $\psi_1^* (H_1 [H_2 \psi_2])$ (serious error).

In the equation next to (109) replace $\frac{dF}{dt}$ by $\frac{d\bar{F}}{dt}$ and also in eqn (110).

In the line after eqn (111) read for $F = q_i$, $F = p_k$.

In the first eqn of (114), H & q_k must be written as operators on the right hand side also.

In the line below eqn (116) replace H by $\bar{H}$.

" eqn above " " " the first term in sq. brackets should have $\frac{\partial \psi}{\partial q_{1k}}$ in lieu of $\partial/\partial q_{1k}$

In the equation after (119) in the first term replace dV by dq. The same is true of eqn (75').

The eqn below (117") must be denoted as (120).

In eqn (121') replace n by N.

In third line after eqn (121') replace (107) by (110).

It is more reasonable to call eqn (97*) as (98'$_1$) - Similarly on p. 121, use (98"$_2$) & (98"'$_3$).

In the eqn for i_x, in the first term within sq. brackets replace φ by ψ.

In " for $p_x \psi$ below the V.R, ψ should not be within the square root

2. In eqn (127) the first factor in the integrand should be $\bar{u}^*_{\lambda',\lambda''}$ (4)

4. The Schrodinger eqn as written on this page must have the first 2 terms + ve.

7. Eqn (131') is not indicated – it is perhaps $\int u_n^* v_n \, dq = 1$

" (132) " – " $f \sim a_1 u_1 + \cdots + a_n u_n + \cdots$

In the line above the equation next to (132'), replace (132) by (132').

8. Eqn (131') must be eqn (131") and in this equation 1st factor in the integrand is $\bar{u}^*$

Eqn (135) similar correction in the first factor in integrand

(137) " second " "

In this page eqn (139') must be called (139").

In (II) line $\lambda' \to \lambda^*$ must be $\lambda' \to \lambda$.

Eqn (147), for the first and second integrals introduce limits λ_1, λ_2

In the reference above in the line two places above the formula above (153) read (134')

instead of (133').

Line after eqn (153), ~~(134) must be (134')~~ instead of (134) read (151).

Line after eqn (158') instead of (141') have "I in (158')

In the next line v_n should be replaced by u_n.

~~In eqn (164), S^*_{lm} should be replaced by S_{lm}~~

In text in small type in the expn for $[\underline{\underline{S}} f(r)]$ $\Sigma a_k v_k(r)$ should be $\Sigma a_l v_l(r)$.

eqn (164) second one to be (164') and third one to be (164").

Third line after (164') should have $\underline{\underline{F}}'$ instead of F'

Two lines below (165), both p's should be replaced by one p & one q.

Two lines after (166') ref. to eqn (148') must be (166').

Last eqn but one, second term inside integral should be $\phi_n^* (\underline{\underline{F}} \underline{\underline{H}} \phi_m)$ – ~~for this relation~~

~~it should be hermiticity of F does not appear necessary~~

Call eqn (177) as (174')

140. In the line after $U = \underline{\underline{S}}\, e^{\frac{c}{\hbar}\underline{\underline{E}}t}\, \underline{\underline{S}}^{-1}$ replace V by $\bar{U}$.

1. Replace (175) by (173').

Two lines lower replace $\bar{V}$ by $\bar{U}$.

Call the second equation (176) as (173'').

41. Call equation (177) as (173''')

Line below reference (174) ought to be strictly (174').

Call eqn (178) as (181)

" (179) as (181') and in the right hand side of this equation replace $\bar{V}$ by $\bar{U}$.

" (180) as (182), (181) as (182'); (182) as (182'')

In equation (183), ~~Ent~~ must be $E_n t$.

The (*) in the footnote refers to eqn (183) and must be affixed above it.

In eqn (184), Ent must be $E_n t$.

3. In fifth line after (186'') read "inverse" instead of "Universe"

~~Five lines below~~

8. The reference (') in the footnote is inserted in the body of the text. It refers to the first sentence in the last paragraph.

In the line after formula (211), reference (200) should be (210).

Above formula (230_2) reference (230_1) should be (231), or alternatively on p. 153 replace (231_1) by (230_1).

7. Eqn (240_1) in the left hand side $a^{(1)}(t) \to a_m^{(1)}(t)$ & in R.H.S, $a^0(0) \to a_n^0(0)$.
Ω' instead of Ω in 2nd integral in (240_2)

Last line $W(F_1, G_m)$ must be $W(F_n, \bar{G}_m)$.

6. ($232_2'$) appears to be wrong as also ($231_1'$) obvious; $C_{m,k}^{(1)} = -i\, T_{mk}$ and $E_k^{(2)} = -i\,(T\Omega)_{kk}$

7. (231_1) should have $E_m^0 - E_k^0$ in denominator or change (233) into $T_{mk} = -i(\;)$
then ($231_1'$) is correct

Page. 168. In (266a), right hand side must have $m_K \dot{q}_K$ in place $m_K \dot{q}$

" In the line after (268") reference (267) should be (268)

" 177. In the tenth line $u_1 \ldots u_n$ must be $u_1, u_2 \ldots u_h$.

" 178. " fifth " " " " "

" 180. In the line after (290') instead of $l \neq k$, say $i \neq k$.

" " In (291) last term should be $-x_3^{(r)} \frac{\partial}{\partial x_2^{(r)}}$.

182. In the line below $m = m_1 + m_2$, for interval $(-j_1, +j_1)$

183. In (302), first term is $|j_1 - j_2|$

" In (308), second eqn R.H.S must be $\xi_1 \beta + \xi_2 \alpha^*$.

" last line $(\xi_1 \xi^* + \xi_2 \xi_2^*)^r$ must be $(\xi_1 \xi_1^* + \xi_2 \xi_2^*)^r$.

186. Eqn (318') first term in the integral should have $u_n^*(x_3, s_3)$

187. 4th line above (321) ref. to (317) must be to (319).

188. In line below (325') ref (326) to be (325')

189. Line above (326), S_{13} must be S_{23}.

In (326) replace last factor by dS_{N3}.

190. Two lines above (330). for odd fus take $\delta_P = -1$.

" " (328') ref. (326) should be (328)

" " below (330) ref. to (328) " (330)

191. In the eqn for U_a near middle of page, second part should be $\sum_P \delta_P \cdot \frac{P}{\text{①}} u(\,) v(\,)$

193. In the line above (333) ref. to (326) should be (316")

194. 6th line after the formulae at the top have $C_+(S_{13}) C_-(S_{23})$ & $C_+(S_{23}) C_-(S_{13})$

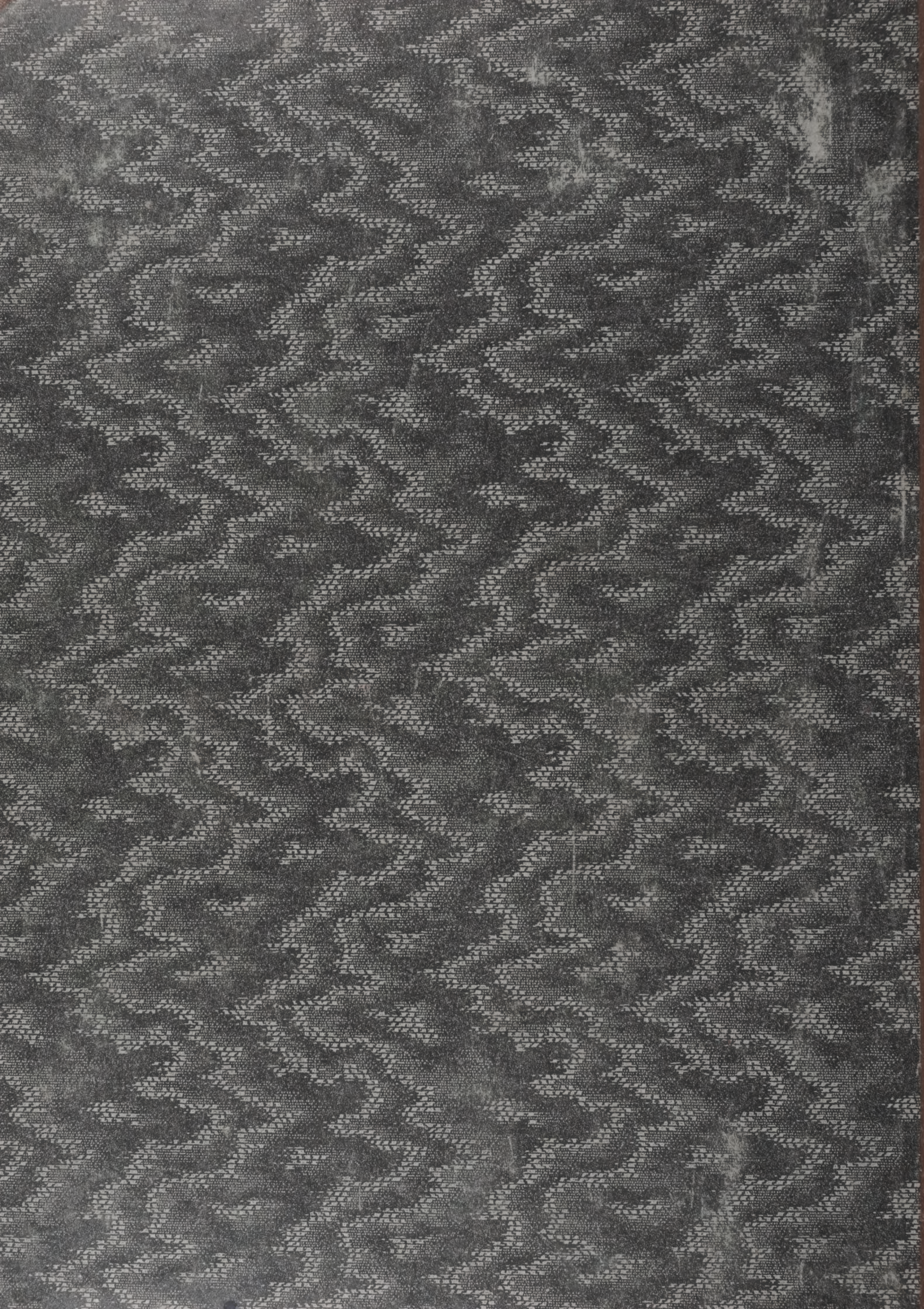
" 3rd line below this have $\delta \equiv 0$ in place of $S = 0$.

" In (335) in J_1 the integrand should have $v^*(x_2) v(x_1)$ in place of $v^*(x_1) v(x_2)$.

197. Line above (337), n^{th} particle should be r^{th} particle.

p. 199 In (342b), all the a's must be replaced α's.

200. In (348') in the second term introduce dq, dq' in the second double integral.

170. In eq^{n} above (272) small c^2 to be capital C^2.

175. In (283, a) first formula R.H.S. e need not be in Clarendon type.